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CVI. *A Molecular Theory of Friction.* *By* G. A. Tomlinson, *B.Sc.* (*of the National Physical Laboratory*) *.

1. IT is now generally agreed that friction is, in some way, a consequence of the forces which molecules exert on one another when sufficiently close together. It is known that two molecules can exert a strong attraction on each other, and there is evidence of various kinds that the field of attraction probably extends to a distance of several times the molecular diameter, the force being a rapidly diminishing inverse function of the distance between the molecules.

Since the molecules of a solid are in a state of equilibrium, we have also to recognize the existence of a repulsive force between them, counteracting the cohesive attraction. There is little or no experimental information concerning this repulsive force, but there is certain indirect evidence that the force increases from zero very abruptly when two atoms approach to a critical distance. The highly stable equilibrium which exists amongst the atoms of a metal can only be explained by supposing that the rate of change of the repulsion is much greater than that of the attraction, when the atoms are drawn apart slightly by an elastic strain. The work of Born and Landé † and others on the energy of the crystal lattice led to similar conclusions. A similar conception has been advanced in recent years by various

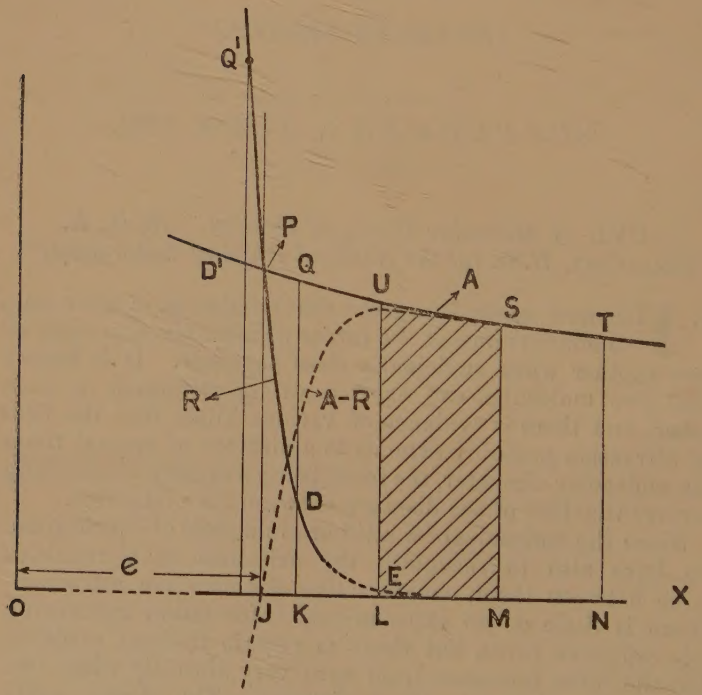
* Communicated by Sir J. Petavel, K.B.E., F.R.S.

† *Deut. Phys. Gesell.* (1918).

other physicists, including Lennard Jones * and T. W. Richards †.

The present paper contains a tentative theory of dry solid friction based upon the assumed existence of molecular attractions and repulsions having such characteristics, as shown diagrammatically in fig. 1 by the curves A and R. These curves represent descriptively the supposed attraction and repulsion as functions of the distance between the mole-

Fig. 1.



cules. No assumptions need be made as to the form of the curves, but the slope of the repulsion curve is assumed to be much greater than that of the attraction curve, and the effective range is supposed to be much less; in fact, considerably smaller than the dimensions of the molecules.

Because of the very limited present knowledge concerning interatomic forces, such a theory must necessarily be to a

* Proc. Roy. Soc. cxii.

† Journ. Amer. Chem. Soc. xlv. to xlviii.

large degree speculative, and its proper place in this paper should be at the end, as a suggested explanation of the experimental work. But although the experiments to be described in the paper may be regarded as having some general interest, they would exhibit no particular connexion with each other, apart from their relation to the tentative theory, the probability of which they were designed to test. It therefore seemed preferable, in order to admit of an adequate seriatim discussion of the results, to give first a preliminary description of the theory, the details of which are further discussed in relation to the several experiments to be described.

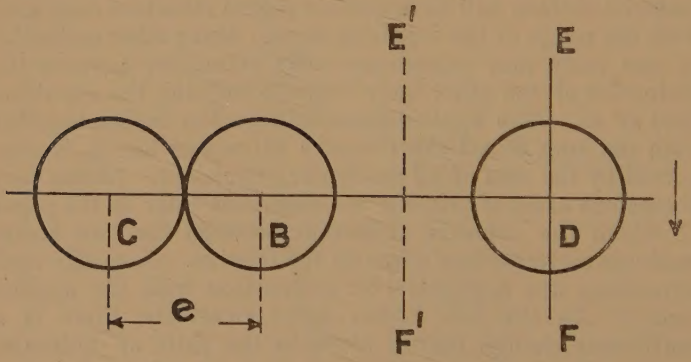
Consider two solid bodies in contact and with relative sliding motion. By our hypothesis, only a certain number of molecules of the one body will approach those of the other body sufficiently closely to suffer repulsion, as any material surface will have quite a coarse structure compared with the range of the repulsive force. Many other molecules of one body may experience some attraction towards the molecules of the other body without entering the repulsion field at all. The applied force between the bodies, together with the sum of all the cohesive attractive forces, is supported by the sum of all molecular repulsions. (Some very anomalous cases of friction are described later in the paper in which the cohesive attraction between the two bodies produces an important effect on the friction. Normally such attractions are negligible by comparison with the applied force.) As the two bodies move relatively, there is a continuous change taking place in the pairs of molecules bearing the load, and the theory assumes that when two molecules come into contact, *i.e.*, come into each other's repulsion field, and then separate, a loss of energy occurs which is manifest as friction. The theory makes no assumptions regarding the cause of the attractive and repulsive forces, but treats the molecules as if they were simple centres of fields of force. Also the ultimate distribution of the lost energy amongst the various possible degrees of freedom is not considered in the theory, which deals solely with the molecular mechanism by which work may become transformed into heat.

It is difficult to understand how friction could be explained as a loss of energy occurring when two atoms approach within each other's attraction field alone. Consider for simplicity a single atom D (fig. 2) forming part of a body which is moving in the direction of E F past another body, of which B and C form two atoms in the state of equilibrium

characteristic of a solid. Referring to the curves A and R of fig. 1, the point P corresponds to the initial undisturbed condition of the atom B, which takes up a position at a distance of O J from C such that the attraction and repulsion on it are equal and opposite and of amount P J. We may observe the very stable condition which follows from the assumed rates of change of the two forces. A small displacement of B in either direction from the point J is accompanied by a strong restoring force.

Let us suppose that the atom D in moving past B along the line E F approaches B to within a distance such as O N in fig. 1; that is, within the attraction field but outside the range of the repulsion. The passage of A will cause a slight disturbance in the position of B, which will move

Fig. 2.



away from C, supposing C to be fixed, to a distance O K in fig. 1 such that the net force Q D now exerted on B by C equals the attraction T N of atom D. The atom D in proceeding further along E F then withdraws from B, which returns to its initial position. It is conceivable that B arrives back to its original position with some appreciable velocity and therefore with some added energy, the aggregate of which might correspond to the loss of energy in friction. If this were the case, however, the energy imparted to B would be reduced as the velocity of relative motion of the two bodies was reduced. But in moving two actual bodies over one another the same total number of atomic approaches would occur whatever the velocity of motion, and therefore the work done, and consequently the coefficient of friction, would be reduced continuously as the velocity was reduced. This is quite contrary to experience. On the other hand, it

known that the characteristic atomic frequency of most of the elements is of the order of 10^{13} per second; and it seems probable that on account of its extremely small natural period, the displacement of the atom B will follow the increase and decrease of the attraction of D in an almost perfectly dead-beat manner. In other words, the mechanical work done on the atom D by the attraction during its approach does not differ materially from the work done by D against the attraction during its recess.

To explain friction it appears necessary to suppose the existence of some irreversible stage in the passage of one atom past another, in which heat energy is developed at the expense of external work. It is possible to suggest a means by which this may happen in the case of those atoms which come near enough together to experience repulsion.

Let us now consider the atom D as passing by the elementary body B C along a nearer line E′ F′ and approaching so close that D and B come into mutual repulsion. As D approaches, the two atoms will exert an increasing attraction, and under this force B will move away slightly from C as before. This process continues until the atoms are separated by a distance O L in fig. 1, at which distance $\frac{dA}{dx} = \frac{dR}{dx}$, A and R denoting the forces of attraction and repulsion. At this period A−R has a maximum value and B is equidistant from D and C. As D approaches still nearer, the symmetrical position of B will be maintained, since for all positions to the left of L, $\frac{dR}{dx}$ exceeds $\frac{dA}{dx}$, and the symmetrical position is one of stable equilibrium. A small movement of D then brings both pairs of molecules into the position corresponding to the point P, *i. e.*, B occupies its original position relative to C with D added to it in a similar stable relationship. Any approach of D now brings into play a powerful net repulsion such as is shown by Q′D′, and this is supposed to be the condition of those molecules which are assisting to support the external load applied to the contact surfaces.

Consider next what occurs when the molecule D is withdrawn. Up to the position corresponding to the point L, the molecule B remains in stable equilibrium equidistant from D and C, and everything up to this point is reversible. At the point L the equilibrium of B changes from a stable into an unstable condition. As this transition is smooth and continuous, there will be a certain probability that the

molecule B will persist in its symmetrical position of equilibrium as D recedes, until B is at some distance O M from both C and D, when, owing to its instability, B will suddenly fly back to its position of stable equilibrium at a point between J and L. This point, in fact, is the same that B occupied when D in its approach was at the same point that it is now supposed to occupy in recess.

The molecule B thus returns to its stable position with a store of kinetic energy equal to the area U S M E, this being the work done on B by D during the irreversible portion of the cycle from L to M. We thus have a possible mechanism by which the recession of two molecules is not the reverse of their approach, but contains an irreversible stage in which mechanical work is transformed into molecular kinetic energy or heat.

According to the theory suggested, friction is in a sense a matter of chance, as the displacement L M of the molecules into the unstable region may vary greatly. Actually we are concerned with the statistical average of a very great number of different values, and the uniformity always observed in experiments on friction is due to the large number of molecules in contact. It may be remarked that on this theory the two bodies in contact become virtually united at all the points where atomic repulsion occurs, by the formation of a continuous chain of atoms in stable equilibrium. On severing the atomic bond the plucking action of one atom on the other dissipates a quantity of energy which is independent of the velocity of relative motion, and in this respect the theory is in agreement with experiment. Further, only those atoms which contribute to the elastic reaction, and so help for a short time to support the load, pass through the irreversible stage and so involve friction. This is again in conformity with the fact that the friction is proportional to the load.

In the simple case we have considered in fig. 2 it will be seen to be a matter of chance whether the atom B ultimately attaches itself to C or to D. In the case of actual bodies there seems to be little doubt that the disturbed atom has a strong bias in favour of a return to its original position, and probably nearly all do so. Some, however, definitely do not—a question which is discussed later.

2. We shall next obtain an expression for the coefficient of friction. The force F between the surfaces is supposed to be supported by the sum of the molecular repulsions

$$F = \Sigma (p).$$

Since the force of repulsion varies very rapidly with distance, the individual values of p must vary widely from one place to another and from one instant to another, but a very large number of molecules are concerned under conditions which justify us in assuming the total number n to be statistically constant so long as the load is constant. This being so, we can assign a statistical average value $\bar{p}$ to the force of repulsion of a pair of molecules, and we then have

$$\mathrm{F} = n\bar{p}.$$

The actual value of n will depend on the total load and the shape of the contact surfaces.

As one body slides over the other, a continuous exchange of partners will proceed amongst the repelling molecules. Some will pass out of the repulsion range and others will enter it. At each approach and separation a loss of energy occurs, of which the average value will be called W.

If we can find an expression for the total number N of separations taking place in a movement x, we can equate the loss of energy to the external work done :

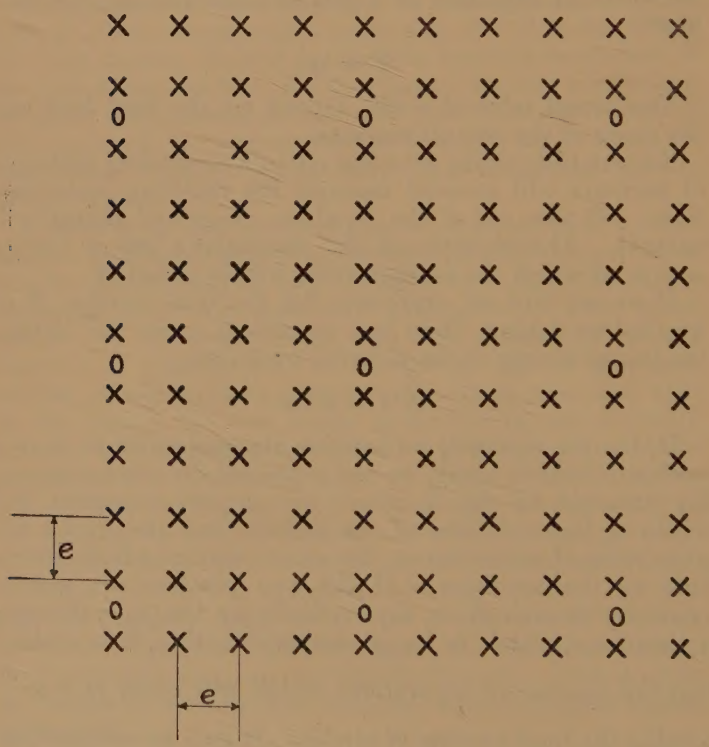
$$\mathrm{NW} = \mu \mathrm{F}x.$$

If, for the moment, we imagine the molecules to have a perfectly definite array, we can represent the circumstances, for example, by fig. 3, where the crosses represent the whole of the molecules of one surface, and the circles the proportion of molecules on the second surface which contribute to the repulsion. If the two patterns are moved relatively to each other, say vertically up the page, through a distance x, which is large compared with e, it is evident that the number of separations which will occur is $n \times \frac{x}{e}$ n being the total number of circles. It may be noticed that in the theoretically ideal distribution shown in the figure we should get a different number of separations if the relative motion of the two bodies were in a different direction—*e. g.*, if the motion were at 45°, the number would be $n \times \frac{x}{\sqrt{2}e}$. There is some evidence, as a matter of fact, that friction between crystalline surfaces may depend on the direction of relative motion.

In any ordinary case, however, the general distribution of the molecules in the surfaces and of the individual molecules concerned in the repulsion at any moment will be quite

irregular, and we assume, moreover, that the surfaces will have a coarse structure in comparison with the extent of the repulsive field. There must, however, be a sufficient number of molecules within the repulsive range at any moment to support the load, and the conditions will be statistically

Fig. 3.



constant, so that we may reasonably assume that the number of separations in distance x will be

$$N = q \times n \times \frac{x}{e},$$

where e is the *mean* molecular distance and q a statistics constant whose actual value must remain unknown, but probably not very widely different from unity.

We then have

$$NW = \mu F x = \mu n p x,$$

also $$NW = q\frac{nx}{e}W,$$

and hence $$\mu = \frac{qW}{\bar{p}e}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Remembering our initial assumptions as to the nature of the molecular attraction and repulsion, we can express W approximately in terms of the normal cohesive attraction and the average displacement $\bar{l}$ of the molecule into the unstable region of equilibrium (LM of fig. 1). Thus, if we take the force of attraction acting over the small displacement $\bar{l}$ to be a constant force A_0 slightly smaller than the normal cohesion P J of fig. 1, and neglect the small repulsive force acting between L and M, we get as a somewhat free approximation

$$W = A_0\bar{l}$$

and $$\mu = q\frac{A_0\bar{l}}{\bar{p}e}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

a form of expression of more interest than (1).

The result obtained from the theory is so far in agreement with the experimental laws of friction ; viz., that the friction is proportional to the load, independent of the area in contact and independent of the velocity of motion.

Further, in the expression for μ, A_0 and $\bar{p}$ may be regarded as molecular elastic constants which must have some association with the ordinary elastic constants of the material. The theory therefore suggests that the coefficient of friction should be related to the elastic constants. This has been investigated experimentally and a definite relation discovered. A discussion of this follows in section 8.

3. The foregoing theory will now be applied to the case of rolling friction. Consider a cylinder of radius r and length b rolling through a distance x on a horizontal plane surface under a load F. Let P be the force to be applied at the axis of the cylinder parallel to the plane to overcome the friction. Then the coefficient of rolling friction will be defined as

$$\lambda = \frac{P}{F}.$$

Making the same assumptions as before, we require to find the total number of molecular separations which occur in rolling a distance x. It is known that the cylinder and

plane come into contact over a parallel strip of width $2a$ which can be determined. The intensity of normal stress is a maximum at the centre of the strip, and falls off to zero at the edges according to the equation

$$\left.\begin{aligned} f &= \frac{3}{2} f_{\text{mean}} \sqrt{1-\frac{y^2}{a^2}} \\ &= \frac{3}{2}\frac{\mathrm{F}}{2ab} \sqrt{1-\frac{y^2}{a^2}} \end{aligned}\right\}, \quad \ldots \quad (3)$$

where y is the distance from the centre of the strip.

The maximum stress intensity at the centre strip is thus

$$f_{\text{max.}} = \frac{3}{4}\frac{\mathrm{F}}{ab}. \quad \ldots \quad (4)$$

In rolling a distance x a rectangular area bx is swept out, and every portion of this area comes in turn under the normal stress $f_{\text{max.}}$ Small end-effects are rendered negligible if b and x are supposed to be large in comparison with a. Hence the aggregate force which is applied and removed is

$$\frac{3}{4}\frac{\mathrm{F}}{ab} bx = \frac{3}{4}\frac{\mathrm{F}x}{a}.$$

If we had again the ideal geometrical arrangement of molecules in rows, the number of separations associated with the application and removal of this load would be given by the equation

$$n\bar{p} = \frac{3}{4}\frac{\mathrm{F}x}{a}.$$

But as the surfaces in contact are continuously changing by the rolling motion just as in the preceding section they were changed by sliding, and the same irregular distribution of the repulsions exists, the actual number of separations will be qn, q being the same statistical factor as before, since both sliding and rolling have the similar effect of bringing a sequence of different but statistically equivalent molecular distributions into contact.

Hence the loss of energy

$$\begin{aligned} &= \tfrac{1}{2} qn\mathrm{W} \\ &= \frac{3}{4}\frac{\mathrm{F}x}{a\bar{p}} q\mathrm{W} \\ &= \frac{3}{4}\frac{\mathrm{F}xq}{a\bar{p}} \mathrm{A}_0\bar{l}. \end{aligned}$$

Equating this to the external work done,

$$P x = \lambda F x = \frac{3}{4} \frac{F x q}{a p} A_0 \bar{l}.$$

Or
$$\lambda = \frac{3}{4} \frac{q A_0 \bar{l}}{a p} \quad \ldots \ldots \ldots \quad (5)$$

This expression for the coefficient of rolling friction is very similar in form to equation (2) for the coefficient of sliding friction. In fact, by the present theory rolling and sliding friction are regarded as being identical in nature, a question which is discussed at more length in section 9.

4. The theory of friction outlined above is admittedly somewhat abstract and speculative. It is a remarkable fact, however, that a phenomenon so universal and important as the friction between solid bodies has so far received no satisfactory explanation. This, together with the fact that the present theory is supported in a number of ways by the results of experiment, appears to justify its presentation as a tentative explanation of friction. The experimental work will now be reviewed.

In the first place it may be noticed that the two expressions which have been derived from μ and λ each contain certain quite unknown quantities q, A_0, $\bar{p}$, and l. If, however, we take the ratio of λ and μ we get

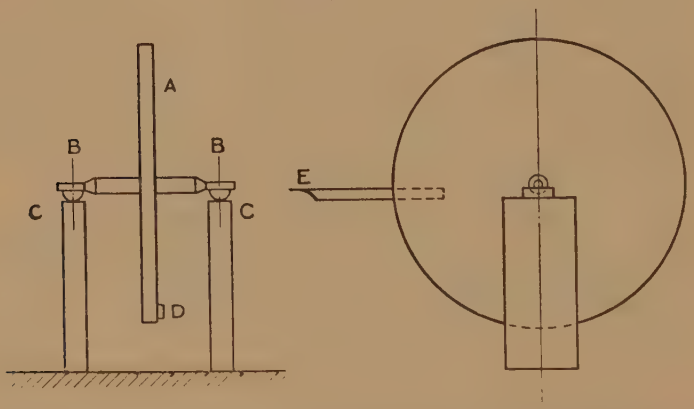
$$\frac{\lambda}{\mu} = \frac{3}{4} \frac{e}{a}, \quad \ldots \ldots \ldots \quad (6)$$

in which all the unknown terms disappear, and a definite relation between λ and μ is obtained. In order to test this relation by experiment, the coefficient of rolling friction in a particular case was carefully determined. For this purpose a ground-steel disk A (fig. 4) was mounted on a spindle having hardened ends B ground and lapped to a diameter of 0·1 in. These lapped ends rested on two hard steel pads C in the form of semi-cylinders with the plane lapped face uppermost. The axes of the two pads were placed at right angles to the axis of the spindle, this geometrical arrangement ensuring that the bearing of the spindle on the flat face is uniform. This disk was given a small oscillatory motion rolling on the two pads. A small mass D was attached to the disk so that it could make slow vibrations as a pendulum. A light pointer E was attached to the disk, and an image of this was projected on to a screen magnified 50 times. With

the disk oscillating slowly the successive semi-amplitudes were marked off at the rest positions of the image of the pointer on the screen. In this way the decrement of the amplitude was accurately measured, and from this friction could be found. The resistance of the air was examined by conducting a similar experiment having the disk suspended with its axis vertical on a torsional suspension of piano wire, giving the same frequency of oscillation. It was found that the contribution of the air resistance to the total friction measured in the rolling experiments was negligible. The rolling surfaces were thoroughly cleaned with alcohol-ether-ammonia cleaning mixture before the measurement.

The results obtained are given in Table I.

Fig. 4.



The theoretical relation in equation (6) may be used to calculate λ in terms of μ, for comparison with the above experimental result. As regards the value of e, the distance between the atoms, X-ray measurements give the lattice constant of iron to be $2{\cdot}86 \times 10^{-8}$ cm., and this value will be used for e.

The value of $2a$ can be found from equation (7) following, and is given in Table I.

$$\text{Hence} \qquad \frac{\lambda}{\mu} = \frac{3 \times 2{\cdot}86 \times 10^{-8}}{4 \times 4{\cdot}14 \times 10^{-4}} = 0{\cdot}519 - 10^{-4}.$$

For clean dry steel Sir William Hardy has found $\mu = 0{\cdot}79$, and the writer has obtained a value 0·39 (see Table VI.): substituting these values, λ is found to be 0·000041 or 0·000020 respectively. If these are compared with the

first three observed values of λ in Table I., a satisfactory order of agreement is found, especially in the case of the higher value of μ. It is considered preferable to exclude the last two observed values from this comparison, for reasons discussed later in section 6.

TABLE I.

Diameter of cylinders 0·1000 in.
Length of cylinders in rolling contact 0·100 in.
Total weight 600 gm.
Width of contact area, $2a = 8{\cdot}28 \times 10^{-4}$ cm.

Amplitude of oscillation.		Coefficient of friction. λ.
cm.	radians.	
0·0090	0·0707	0·000047
0·00506	0·0398	0·000041
0·00135	0·0106	0·000045
0·00038	0·0030	0·000015
0·00024	0·0019	0·000011

5. Some further experimental results on rolling friction will now be examined, and will be shown to be in close agreement with the theoretical expression deduced for the coefficient. The quantity a which occurs in this expression can be found from the equation given by Hertz in his theory of elastic contact :

$$a^2 = \frac{1}{\pi} \mathrm{F} r (\vartheta_a + \vartheta_b) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where

r = radius of cylinder,

F = load on the cylinder per unit length,

$$\vartheta = \frac{3\mathrm{K} + 4\mathrm{C}}{\mathrm{C}(3\mathrm{K} + \mathrm{C})},$$

C = modulus of rigidity,

K = modulus of compressibility.

The suffixes a and b refer to the two materials forming the roller and the plane.

Where these are both the same we have

$$a^2 = \frac{2}{\pi} \mathrm{F} r \vartheta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Hence, using equation (6), which is cleared of all the unknown terms, for the value of λ in terms of μ, we have

$$\lambda = \frac{3}{4} \frac{e\mu}{a} = \frac{3}{4} \sqrt{\frac{\pi}{2}} \frac{e\mu}{\sqrt{\mathrm{F} r \vartheta}}. \quad . \quad . \quad . \quad . \quad (9)$$

This equation indicates that λ is not a constant, but is inversely proportional to $\sqrt{\mathrm{F}}$ and to $\sqrt{r}$.

Goodman * carried out an extensive investigation on

Table II.

Load F in lb.	Coefficient of rolling friction.	Coefficient of friction $\times \sqrt{\mathrm{F}}$.
1000.....	0·0040	0·1265
2000.....	0·0028	0·1252
3000.....	0 0023	0·1260
4000.....	0·0020	0·1264
5000.....	0·0018	0·1273
6000.....	0·0016	0·1239
7000.....	0·0015	0·1254
8000.....	0·0017	0·1520
9000.....	0·0017	0·1613
10,000.....	0·0018	0·1800

rolling friction, employing commercial ball and roller bearings, and he arrived at the following conclusions :—

(1) The coefficient of friction decreases as the load increases.

(2) The coefficient of friction decreases as the radius increases.

(3) The coefficient of friction is nearly independent of the speed.

These conclusions agree qualitatively with equation (9), but the theory can be tested further as regards the variation of the coefficient of friction with load by comparison with Goodman's results. In Table II. the first two columns are

* Proc. Inst. Civil Eng. 1911-12.

taken from Goodman's paper, and the third column has been computed by the writer. The measurements were made on a roller bearing having rollers $\frac{3}{4}$ in. in diameter and 6 in. in length. The speed of the shaft was 80 revolutions per minute and the bearing was run without lubricant.

The last column shows that over a wide range of loads the theoretical relation between the load and the coefficient of friction is in very good agreement with the experimental results.

6. If the foregoing theory of friction is substantially correct an interesting deduction may be made. If two surfaces have a relative oscillatory motion, either sliding or rolling, and it is possible to reduce the amplitude to such an extent that the displacement of the surfaces or some portion of them becomes comparable with $\bar{l}$, we should find that an increasing proportion of the molecules would return through the unstable stage to the stable condition of equilibrium without being released with increased kinetic energy. Or we should expect the friction to become progressively smaller as the amplitude diminishes below a certain value. Such a result has, in fact, been obtained for both sliding and rolling friction in some experiments which will now be described.

A very light oscillator, made from a piece of cork, was pivoted on the point of a fine needle on a polished steel flat surface. A small piece of mirror was attached to the cork and also a piece of magnetized sewing-needle to provide a suitable control couple. The oscillator was contained in an exhausted vessel having a plate-glass window. The oscillations were observed by a reflected image of a cross-line on a remote scale. An oscillation was started by disturbing the magnetic field slightly, and the successive amplitudes were measured at the scale.

It can be shown that the amplitude will decrease uniformly if friction is constant. Thus let θ_1 und θ_2 be two successive amplitudes. Then the energy lost in friction is

$$c(\theta_1+\theta_2),$$

where c is a constant.

This is equal to the change in potential energy of the system, or

$$c(\theta_1+\theta_2)=\tfrac{1}{2}k(\theta_1^2-\theta_2^2),$$

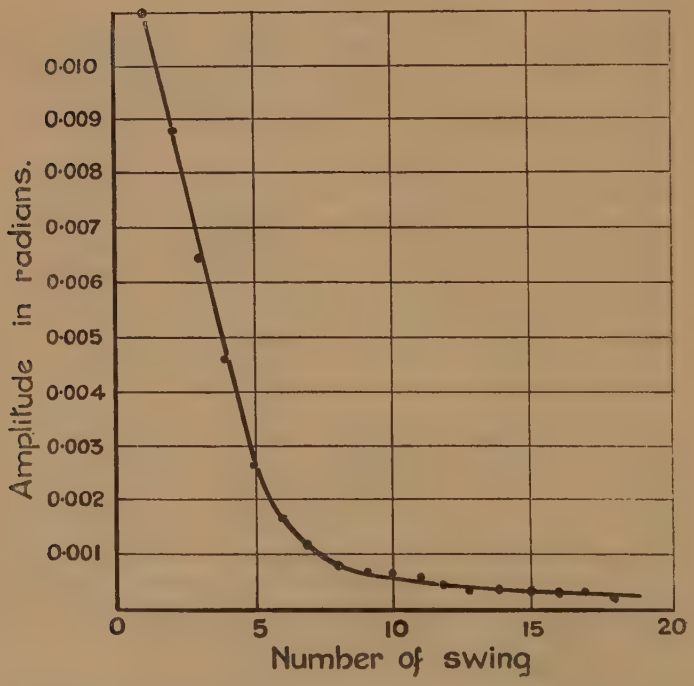
where k is the stiffness of the controlling couple.

Hence $$\theta_1-\theta_2=\frac{2c}{k}=\text{constant}.$$

The actual result obtained is very different, as shown by the curve in fig. 5, in which there is a well-defined deviation from the straight line at a certain amplitude, followed by a rapidly diminishing friction couple.

It is interesting to make an estimate of the relative linear displacement of the surfaces corresponding to the knee of the curve.

Fig. 5.



In an investigation into the deformation of instrument pivots at the National Physical Laboratory, Stott has found that a small flat is produced, the area of which over a wide range of loads is proportional to the load, or a definite flow-stress exists which is constant for any load. The value of this stress is found by Stott to depend somewhat on the angle of the pivot, and for the present purpose an assumed stress of 500 kilogrammes per square millimetre will be a fairly probable value. The weight of the oscillator was 0·15 gm., and the radius of the small flat, if it is assumed to be circular, is therefore about 3×10^{-5} cm

The bend in the curve corresponds approximately to an amplitude of about 0·0015 radian, so that the motion at the edge of the contact flat is about $4{\cdot}5 \times 10^{-8}$ cm. This is an amount of nearly the same magnitude as the distance between the atoms as found by X-ray measurements. The linear motion decreases uniformly to zero from the periphery to the centre, and the reduction in friction probably commences at the centre of the compressed area, spreading outwards more and more as the amplitude decays away. Hence the critical amplitude at which the friction begins to diminish is apparently an amount well below atomic dimensions.

TABLE III.

Rolling friction of two crossed cylinders 0·1 in. and 0·4 in. diameter.
Total weight 600 gm.
Major semi-axis of contact of ellipse, $5{\cdot}95 \times 10^{-3}$ cm.
Minor semi-axis of contact of ellipse, $2{\cdot}4 \times 10^{-3}$ cm.

Amplitude of oscillation.		Coefficient of friction. λ.
cm.	radians.	
0·00845	0·0665	0·000014
0·00720	0·0567	0·000013
0·00561	0·0442	0·000012
0·00276	0·0217	0·000010
0·000635	0·0050	0·000006
0·000237	0·00187	0·000004

In the case of rolling friction a similar result has already been obtained, as shown in Table I., where the coefficient of rolling friction decreases to about a quarter of its initial value when the amplitude becomes very small. This decrease was always observed in measurements of λ, and two further examples are given in Tables III. and IV. In the first case the 0·1 in. diameter cylinders are rolling upon two other cylinders of 0·4 in. diameter set at right angles to the axis of rolling.

In the second case two $3\frac{1}{2}$-mm. steel balls are rolling on flat steel surfaces.

7. The measured coefficients of friction for three different types of rolling, given in Tables I., III., and IV., can be compared with the relative values of the coefficients found from the theoretical expression for λ, as a further test of the probable validity of the theory.

It will first be shown that equation (5) applies equally in all these cases of rolling.

In general, the contact area is an ellipse having semi-axes, b, parallel to the axis of rolling, and a, parallel to the

TABLE IV.

Rolling friction of $3\frac{1}{2}$-mm. steel ball on steel plane.
Total weight 600 gm.
Radius of contact circle, $3{\cdot}3\times10^{-3}$ cm.

Amplitude of oscillation.		Coefficient of friction. λ.
cms.	radians.	
0·0077	0·0605	0·0000165
0·0067	0·0528	0·0000155
0·00404	0·0318	0·0000125
0·00086	0·00675	0·0000048
0·000442	0·00348	0·0000030
0·000232	0·00183	0·0000017

path of rolling. Let a and b correspond to X and Y axes respectively, then the normal contact-stress is given by

$$f=\frac{3}{2}\frac{\mathrm{F}}{\pi ab}\sqrt{1-\frac{x^2}{a^2}-\frac{y^2}{b^2}}, \quad . \quad . \quad . \quad . \quad (10)$$

and the mean stress along the Y axis, parallel to the axis of rotation, is

$$\frac{\int_0 f\,dy}{\int_0^b dy}=\frac{\frac{3}{2}\frac{\mathrm{F}}{\pi ab}\int_0^b\sqrt{1-\frac{y^2}{b^2}}\,dy}{b}$$

$$=\frac{3}{8}\frac{\mathrm{F}}{ab}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Hence, as in section 3, the total load applied and removed in rolling through a distance x is

$$2bx \times \frac{3}{8}\frac{F}{ab} = \frac{3}{4}\frac{Fx}{a}, \quad . \quad . \quad . \quad . \quad . \quad (12)$$

which is the same result as that previously obtained for the rolling of a cylinder on a plane, that being only a particular case.

According to the theory, therefore, the relative coefficients of friction should be inversely proportional to the values of a. These have been calculated, and the results are summarized below.

TABLE V.

Type of rolling.	a. cm.	Theoretical, λ.	Measured, λ.
A. Cylinder on plane	$4{\cdot}14\times10^{-4}$	0·000041	0·000047
B. Cylinders on cylinders...	24×10^{-4}	0·000007	0·000013
C. Spheres on plane	33×10^{-4}	0·000005	0·000016

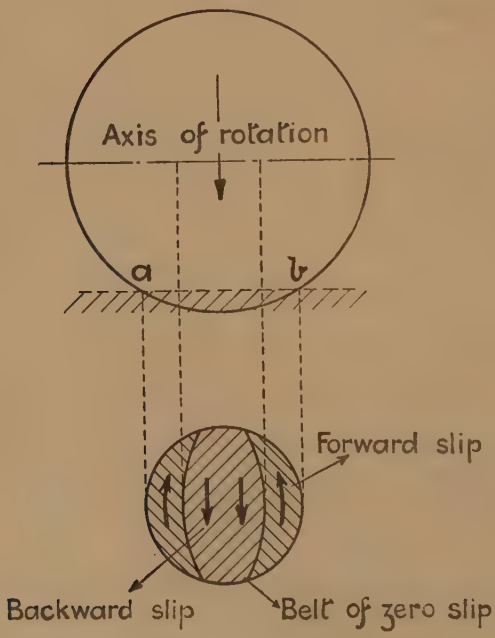
The theory thus shows that the rolling friction in cases B and C should be about $\frac{1}{6}$ and $\frac{1}{8}$ respectively of that of case A. Although the measured values are considerably smaller, there is some discrepancy in the relative values as compared with the theoretical values. These is reason for this, however, in the fact that cases B and C are not exactly examples of pure rolling.

Heathcote * has pointed out in connexion with the friction of ball bearings that some relative sliding motion must take place continuously at the contact. In fig. 6 a sphere rolling on a plane is shown. Different parts of the sphere between a and b are at slightly different radii from the axis of rotation, and therefore must have different peripheral velocities, leading to a distribution of relative sliding somewhat as shown in the diagram. There are two symmetrically-placed belts along which no slipping occurs, and inside the belts the surface of the ball slips backwards, while outside the belts the slip is forwards. The form of these belts shown is purely conjectural, but their existence has been demonstrated

* Proc. Inst. Auto. Eng. xv.

by Heathcote. The rolling action in case C is therefore not pure rolling such as occurs in case A, and there is an additional source of friction present which will tend to increase the measured coefficient of rolling friction above the theoretical value. In case B a similar effect is present, but probably to a less extent when a small cylinder rolls on a large one. Unfortunately this additional friction cannot be computed; but if we recognize its presence, the results of Table V. are in reasonable conformity with those indicated by the theory.

Fig. 6.



8. The expression $q\frac{A_0}{p}\frac{l}{e}$ for the coefficient of friction suggests, as previously remarked, that μ may be related to the elastic constants in some way. This possibility will now be examined more closely. Consider, for simplicity, a sphere of one material A sliding on a plane of another material B to which we can apply Hertz's equations for elastic deformation. In the present theory, friction is supposed to be proportional to the number of molecules undergoing repulsion, and at the same time this number is supposed to

be proportional to the load, these suppositions leading to agreement with the well-known fundamental law of friction.

For a load F and radius r, Hertz shows that the contact circle has an area

$$\alpha \propto F^{\frac{2}{3}} r^{\frac{2}{3}} (\vartheta_A + \vartheta_B)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

As we are at present only concerned with the nature of the material, we shall in the first place simplify the reasoning by regarding F and r as constant, under which conditions

$$\alpha \propto (\vartheta_A + \vartheta_B)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

In the theory it is assumed that

$$F = n\bar{p},$$

and in the case of a soft material the maximum repulsion between two molecules will be small, not because the molecules are incapable of exerting greater repulsion, but rather because the lattice strength will not support any greater force without distortion. Hence for the soft material the mean repulsion $\bar{p}$ will also be small, and to support the load F the number of molecules must be correspondingly large. In terms of elasticity the more yielding material has a high value of ϑ and a large contact area α.

For the given load F the value of n is inversely proportional to $\bar{p}$. But the coefficient of friction by equation (2) should also be inversely proportional to $\bar{p}$ and therefore directly proportional to n, where different materials are concerned, or, substituting in equation (2),

$$\mu = \frac{q A_0 \bar{l} n}{Fe}.$$

If, as we may reasonably assume, there is some simple relation for various materials between the molecular quantity n and the elastic quantity α, we may write n as some function of α, let us say $f(\alpha)$.

Hence $$\mu \propto \frac{q A_0 \bar{l}}{Fe} f (\vartheta_A + \vartheta_B)^{\frac{2}{3}},$$

and we may therefore expect to find some systematic connexion between μ and $(\vartheta_A + \vartheta_B)^{\frac{2}{3}}$. It has actually been found from the measurement of a large number of coefficients of friction that μ is directly proportional to $(\vartheta_{A+B})^{\frac{2}{3}}$ with a fair degree of exactness.

Before describing these experiments we shall briefly consider the meaning of this experimental result. It follows

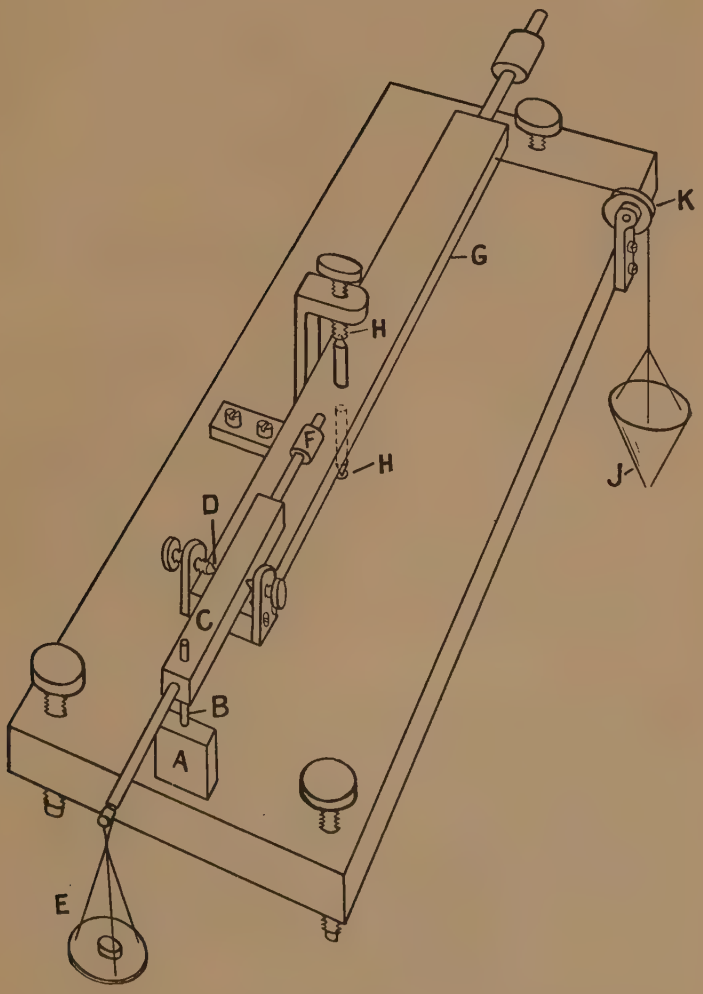
in general that the harder the two materials are the smaller the coefficient of friction will be. Also, since in the present argument F is a constant and q may be assumed to have a similar value for any material, the quantity $\frac{A_0\bar{l}}{e}$ can be regarded as the same for all the different materials used. The atomic distance e does not vary greatly amongst the different metals; hence $A_0\bar{l}$, which represents the loss of energy in a single molecular separation, is roughly constant. This deduction appears to be not illogical on general grounds, for when the molecular cohesion bond is weak, that is A_0 is small, one would expect the displacement of the molecule beyond its limiting stable position to be greater.

The available data on dry friction were found to be somewhat meagre; and as this relation has a very important bearing on the present theory, a fairly extensive series of coefficients of friction has been measured. In this series ten different materials were used in all the possible combinations, yielding altogether 55 different coefficients of friction. The apparatus used for the purpose is shown by a perspective sketch in fig. 7. A plane surface A of one of the two materials has a spherical end B of a rod of the other material in sliding contact with it. The rod is carried by a lever C pivoted about a horizontal axis on hardened steel points D. A light scale-pan E is suspended from the free end of this lever, and the whole can be balanced by a counterpoise weight F. The supports for the pivot are themselves attached to a second lever G, which is similarly pivoted about a vertical axis on points H. A known normal load can be applied by weights in the pan E, and the tangential friction force is applied by feeding a fine stream of silver sand into a paper hopper J, which is attached to the lever G by a thread of cotton passing over a light pulley K. The effect of the friction of the various pivots on the results was found to be quite negligible, all the pivots being carefully prepared on a special pivot lapping machine in use at the National Physical Laboratory. The apparatus can be balanced and levelled so that the lever G floats freely in any position.

The contact surfaces, when of metal, were worked up on the finest grade of blue-black emery paper and finally polished on wet chamois leather. The surface was washed with a cleaning fluid and scrubbed with a pad of specially pure cotton-wool until a clinging contact was obtained and the surface emitted a continuous squeaking noise under the

motion of the pad. In the case of lead the surfaces could not be polished and cleaned in the above way, and cleanness

Fig. 7.



was ensured by working with a freshly-cut surface of the metal, prepared by paring it with a clean razor blade. With glass a fused spherical slider and a piece of plate glass were used.

The measured coefficients of friction are given in Table VI., and in Table VII. the computed values of the ratio

$$\frac{(\vartheta_A+\vartheta_B)^{\frac{2}{3}}}{\mu}\times 10^8$$

are given. An inspection of Table VII. shows this ratio to be nearly constant. The mean value is $5{\cdot}47\times10^{-8}$, and 42 of the 55 values lie within about 10 per cent. of the mean. If the mean value of the ratio is found for each material when paired in turn with all the materials, the constancy is even more striking. These mean values are shown in the last row.

The experimental results thus show that the coefficient of friction of any two surfaces is not a fortuitous constant, but is a function of the elastic moduli K and C, and may be expressed with a fair degree of accuracy by an equation,

$$\mu = 0{\cdot}18\times10^8\,(\vartheta_A+\vartheta_B)^{\frac{2}{3}}.$$

As regards their bearing on the theory of friction, these results certainly appear to support the assumption that the number of molecules in repulsion adjusts itself to be proportional to the load, and that the friction is proportional to this number. It should be made clear that, although the coefficient of friction is found proportional to the contact area in the restricted case of equation (14), it is not to be understood that this applies in the general case of equation (13). In other words, the number of molecules in contact is not proportional to the total area, the number per unit area being a function of the radius of curvature and of the actual load applied, as might be expected, since the intensity of normal stress depends on these variables.

The series of coefficients of friction in Table VI. is in itself of some interest. It will be seen that the values found for any one material taken in turn with all of the materials are in ascending order of magnitude, which is the same for every material. Also, where any two materials A and B are concerned, the coefficient μ_{ab} is nearly always intermediate between μ_{aa} and μ_{bb}. These results of course follow at once from the more general relation,

$$\mu \propto (\vartheta_A+\vartheta_B)^{\frac{2}{3}}.$$

9. There is no theory of sliding friction which has general acceptance, but in the case of rolling friction a theory was developed by Osborne Reynolds * which has been considered

* Phil. Trans. Roy. Soc. lxvii.

Table VI.

	Hard steel.	Mild steel.	Platinum.	Nickel.	Copper.	Brass.	Aluminium.	Glass.	Tin.	Lead.
Hard steel	·393	·410	·398	·428	·548	·535	·649	·605	·785	1·955
Mild steel.....	·410	·411	·427	·429	·533	·506	·605	·721	·786	1·930
Platinum	·398	·427	·445	·386	·592	·560	·796	·569	·855	2·070
Nickel	·428	·429	·386	·389	·562	·504	·745	·775	·895	2·150
Copper	·548	·533	·592	·562	·600	·618	·695	675	·857	1·945
Brass	·535	·508	·560	·504	·618	·634	·706	·873	·752	2·110
Aluminium	·649	·605	·796	·745	·695	·706	·937	·845	·905	2·000
Glass	·605	·721	·569	·775	·675	·873	·845	·940	·941	2·420
Tin	·786	·786	·855	·895	·857	·752	·905	·941	1·110	2·250
Lead	1·955	1·930	2·070	2·150	1·945	2·110	2·000	2·420	2·250	3·310

Table VII.

	Hard steel.	Mild steel.	Platinum.	Nickel.	Copper.	Brass.	Aluminium.	Glass.	Tin.	Lead.	C dynes per sq. cm.	K dynes per sq. cm.
Hard steel...	5·55	5·47	5·97	5·32	5·20	5·71	5·38	6·12	5·19	5·23	$8·9\times10^{11}$	$18·0\times10^{11}$
Mild steel .	5·47	5·64	5·69	5·44	5·43	6·14	5·89	5·20	5·29	5·36	8·1	16·4
Platinum ..	5·97	5·69	5·70	6·29	5·09	5·73	4·58	5·56	4·94	5·02	6·1	24·7
Nickel	5·32	5·44	6·29	6·03	5·18	6·19	4·81	4·85	4·63	4·81	7·7	17·6
Copper	5·20	5·43	5·09	5·18	5·79	5·88	5·80	6·24	5·35	5·44	4·0	13·6
Brass	5·71	6·14	5·73	6·19	5·88	6·02	5·98	5·03	6·02	5·10	3·5	10·6
Aluminium .	5·38	5·89	4·58	4·81	5·80	5·98	4·94	5·65	5·65	5·51	2·7	7·5
Glass	6·12	5·20	5·56	4·85	6·24	5·03	5·65	5·24	5·61	4·60	2·9	4·0
Tin	4·19	5·29	4·94	4·63	5·35	6·02	5·65	5·61	5·06	5·10	2·05	5·3
Lead	5·23	5·36	5·02	4·81	5·44	5·10	5·51	4·60	5·10	4·78	0·34	5·0
Mean values.	5·51	5·56	5·57	5·37	5·54	5·78	5·42	5·52	5·29	5·11		

adequate for many years. In the present paper no distinction is made between rolling and sliding friction, both being supposed to arise in the same molecular plucking action. In thus proposing an alternative theory of rolling friction, we are obliged to inquire whether there are any reasons for considering Reynolds's theory inadequate, especially in view of the established character of this theory and the eminence of its author.

According to Reynolds's theory, rolling friction is caused by slight relative tangential motion between the surfaces in contact, due to unequal elastic surface displacements. There is supposed to be a differential creep motion in continuous operation, and this theory thus reduces rolling friction to a particular case of sliding friction. There can be little doubt that this kind of elastic creep does in general occur, with a contribution to the total loss of energy depending on the amount of load. It is the writer's opinion, however, that the amount of this rubbing motion is much too minute to account for more than a small part of the energy lost in rolling, and that this loss is mainly the result of the molecular disturbances which take place on account of the continual shifting of the loaded area. It may be observed that Reynolds's theory is purely descriptive and has never been applied quantitatively, and no criticism as to the accuracy of Reynolds's deductions is now suggested other than modifying the accepted idea of the magnitude of the creep effect and regarding it as only a small contributary cause of friction.

Several reasons can be adduced showing the elastic creep theory to be inadequate. In the first place, reference must be made to some experiments made by the writer at the National Physical Laboratory in connexion with an investigation on rusting of steel surfaces in contact*. It is very well known that when two steel surfaces in close contact have a relative sliding motion, the surfaces become pitted and a brown oxidation product is formed. The same result is found when the surfaces are held tightly together if they are subject to vibration. In this case the only motion occurring is the minute amount due to vibration. In the course of this research it was found that a relative motion as small as 8×10^{-8} inch was quite sufficient to cause rusting. On the other hand, it was found that a prolonged rolling motion never led to any formation of rust at all. We may therefore infer that the differential surface motion in rolling is less

* Proc. Roy. Soc. p. 472 (1927).

than this very small amount. This can be verified by a simple approximate calculation. Taking the case of rolling given in Table I., we can form an estimate of the magnitude of the surface displacement in the contact area. Love * gives an illustration of the lines of principal stress in the neighbourhood of an elastic contact, which shows that the tangential stress over the surface in contact is a compressive stress which changes to a tensile stress on crossing the border of the contact area. It is therefore zero at the edge of the contact area, and the average will be smaller than the maximum. Let us assume that the average tangential elastic strain is 0·001 ; then the displacement of the edge of the contact strip relative to the centre is

$$4{\cdot}14 \times 10^{-4} \times 0{\cdot}001 \text{ cm.}$$

or $$16{\cdot}3 \times 10^{-8} \text{ inch.}$$

We are only concerned in Reynolds's theory with the differential displacement of the two surfaces, which must be considerably smaller than the above value of the total displacement ; hence the calculation roughly bears out the inference from the experiment, that the differential creep does not exceed about 8×10^{-8} inch. Further, the elastic creep is not uniform, but varies between zero and a maximum value at different parts of the contact surface, so that the average creep which is supposed to produce the friction must be a still smaller quantity. It is difficult to understand how such extremely minute relative movement can cause the loss of energy found in rolling, and the difficulty is increased by the fact that the coefficient of sliding friction undergoes a marked diminution at such small amplitudes, as we have shown in section 6.

There are two further arguments which show that Reynolds's theory does not fully account for rolling friction. The first is based on the fact that the coefficient of rolling friction is inversely proportional to the width of the contact area which is demonstrated by both Goodman's and the author's experiments. On Reynolds's theory it appears to be quite impossible to account for this result without arriving at some untenable conclusion as to the relation between the slip and the width of the contact strip. Since the coefficient is known to decrease when the load is increased, it follows that the amount of differential creep in rolling any given distance must decrease when the load is increased. The width of the contact increases with the load in a definite manner;

* 'The Mathematical Theory of Elasticity,' p. 196.

hence we should be forced to the difficult conclusion that the creep decreases as the total arc of contact increases.

The second argument is a simple one. Consider the case of two identical parallel cylinders, one rolling upon the other. In such a case we have perfect symmetry, and the elastic distortions of the two bodies will be exactly alike and the friction in this particular case should on Reynolds's theory be zero, or at least abnormally low, or, if not, some other explanation of the friction must be found. This interesting point was tested by experiment, and the coefficient of friction was determined for parallel cylinders of equal diameter, the lower being stationary with the upper one rolling to and fro upon it. With an amplitude of 0·0188 radian the coefficient was found to be 0·000022, and for direct comparison the friction was then measured after replacing the lower cylinder by a plane surface of the same material and having the same length of contact parallel to the axis of rolling. In the latter experiment with the same amplitude of rolling, the coefficient of friction was found to be 0·000034. The experiment thus shows that the rolling friction of two equal parallel cylinders is not at all exceptionally small, and must arise in some other way than that suggested by Reynolds. It may be remarked that the molecular theory now suggested also offers a simple explanation of the phenomenon described by Reynolds of the oscillation of a roller lying on a plane, if the roller is slightly disturbed. The molecular attractions which the theory supposes are clearly unsymmetrical after a small displacement, and give the resultant restoring couple necessary for an oscillatory rocking motion.

10. One interesting consequence of the molecular theory of friction may be noticed—namely, that by this theory a small loss of energy occurs when two bodies touch with any pressure and separate again in a direction normal to the surfaces; or, in other words, there is some "friction" with purely normal action.

Sir William Hardy has drawn attention to the possibility of this *, but he states that no friction has been detected with normal motion. The loss of energy involved by the present theory is, in fact, so small as to be imperceptible. It can be easily computed as follows. Let the normal pressure exerted be F; then, using the previous notation,

$$F = n\bar{p},$$

* Proc. Roy. Soc. c. (1922).

and the loss of energy is

$$E = n \times A_0 \bar{l}$$

$$= \frac{F A_0 \bar{l}}{\bar{p}}. \quad \ldots\ldots\ldots \quad (15)$$

Using equation (2), this becomes

$$E = \frac{\mu F e}{q}.$$

Thus the loss of energy is proportional to the pressure, and is equal to the work done when the applied force is exerted through a distance $\frac{\mu e}{q}$, an amount comparable with though probably less than the dimensions of the molecules. It is thus not surprising that this loss of energy, if it actually occurs, has not been observed, except as manifested, according to the present theory, in the case of rolling friction, which may be regarded as a continuous process of normal approach and recess.

11. It was remarked in section 1 that when two molecules of actual bodies come into repelling contact and then separate, each molecule has a strong bias to return to its parent body, although momentarily the two are supposed to be in similar equilibrium to that existing within the body of the solid. We shall now discuss this in more detail. The experiments, already referred to, made by the writer on the contact rusting of steel pointed to the conclusion that molecules are torn away by cohesive attraction, and such molecules have a strong affinity for oxygen molecules, the combination giving rise to the brown deposits observed. There is thus definite reason to believe that some of the molecules concerned in contact are detached, and this may be the mechanism of wear.

It can be shown, however, from our knowledge of the ordinary rate of wear of metals, that only a very small proportion of the molecules can be detached.

Each molecule taking part in contact dissipates an amount of energy of average value

$$A_0 \bar{l}.$$

And the mass of the molecule for the present purpose is given closely enough by

$$m = \rho e^3, \quad \ldots\ldots\ldots \quad (16)$$

where ρ is the specific gravity and e is the distance between the molecules.

In dissipating energy in friction of amount E ergs, the number of molecular contacts is therefore

$$N = \frac{E}{A_0 \bar{l}}. \quad . \quad . \quad . \quad . \quad (17)$$

And the mass of all the molecules involved is

$$M = Nm = \frac{E\rho e^3}{A_0 \bar{l}} \quad . \quad . \quad . \quad . \quad (18)$$

From equation (2) we can substitute

$$A_0 \bar{l} = \frac{\mu}{q} \bar{p} e.$$

Whence

$$M = \frac{E\rho e^2 q}{\mu \bar{p}}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

In this expression $\bar{p}$ is unknown and q is of the order of unity, but is otherwise unknown. If, therefore, we can in any way arrive at some reasonable estimate of p and take q as unity, we shall obtain a probable value for the value of M.

The experiments made by Stott on pivots, already referred to, show that a material has a definite flow-stress and is not capable of supporting any stress exceeding this. Mallock * and Hankins † have also independently found somewhat similar results. It will be assumed that this state of flow indicates a condition in which all the available molecules are repelling with the maximum possible force, that is, the limiting force the space-lattice can resist.

If the flow-stress is denoted by f, we then have approximately

$$f = \frac{p_{max}}{e^2}.$$

In a case of elastic contact $\bar{p}$ will be smaller than $p_{max.}$, and if we assume all the possible values of p to be equally probably, $\bar{p}$ will be equal to $\frac{1}{2} p_{max.}$

By taking q as unity, this leads to the following expression for the value of M:

$$M = \frac{2E\rho}{\mu f}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

* 'Nature,' cxvii.

† Proc. Inst. Mech. Eng. (1925).

The value of f found for unhardened steel by Stott is about 250 kilogrammes per square millimetre, and a concrete example will best show that the calculated value of M is very large.

If we consider, for example, a brake horse-power test of a 100 KW. motor dissipating this power for 1 hour by means of a brake on a steel flywheel, then the value of M is of the order 10^7 gram. The actual weight of metal which would be worn away is probably only some small fraction of a gram. Thus, although some very free approximations have been necessary in the above computation, we may quite safely conclude that only an extremely small proportion of those atoms taking part in contact are detached from their original position.

This suggests as an interesting possibility that wear may be fundamentally only an accidental accompaniment of friction. For the purpose of providing an illustration, let us assume the actual wear in the above example to be as much as 1 gram. We may anticipate by remarking that quite a large error in this conjecture does not materially affect the conclusions. On this assumption, only 1 in 10^7 of the molecules effective in causing friction is detached. The total number of molecules which come into contact is

$$N = \frac{M}{m} = \frac{2E}{\mu f e^3}. \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Taking e to be $2{\cdot}86 \times 10^{-8}$ cm., this has a value of about 5×10^{28}, so that the number detached, although only a very small fraction of this, is still a very large number of the order 5×10^{21}. Hence, as in many molecular phenomena, although the wear may be ultimately traceable to the accidental loss of an occasional molecule, the total number involved is so great that uniformity and consistency are always found in the results perceived by measurement.

12. In the course of the experimental work some unusual cases of friction have been encountered which appear to deserve a brief mention. These are instances in which the cohesive attraction of the surface atoms is not negligibly small by comparison with the external force applied between the surfaces in contact. Consequently the normal reaction between the bodies is considerably greater than the applied force, and extraordinary values are obtained for the coefficient of friction, as usually defined.

In one experiment a light slider was used having 3 feet of lead forming an equilateral triangle. The slider was placed on a clean piece of plate glass which could be tilted to any angle. To obtain clean surfaces of lead, the 3 feet were pared away with a clean razor blade. The glass surface and the blade were cleaned by repeated rubbing with a mixture of alcohol, ether, and ammonia. It was found that the plate could then be tilted completely into the vertical position without any slipping of the slider, giving an infinite coefficient of friction by the ordinary definition. Further, with a little care, it was found possible to turn the glass plate round until it was horizontal with the slider in its original position clinging to the under side, showing that the cohesive attraction could exceed the weight of the slider.

Similar results were obtained with two fibres of quartz or glass crossed at right angles. In this case strong cohesive forces can be observed and measured by the elastic deflexion of the fibre, and tangential frictional forces were measured when the applied normal force was zero or even negative, leading to a series of apparent coefficients of friction passing through infinity to negative values.

These experiments illustrate clearly that the coefficient of friction should be defined in terms of the normal reaction between the bodies, rather than in terms of the applied normal force. Otherwise, under certain circumstances, the friction will be far from proportional to the load, and very abnormal values of the coefficient will be obtained.

13. We shall conclude this paper with a short discussion of the fundamental hypothesis that has been assumed concerning the character of the atomic forces of attraction and repulsion. It has been seen in the course of the paper how the various experimental results support the deductions from the theory, even when the theory has indicated certain relations not hitherto recognized, such as the relation between friction and the elastic constants or the relation between sliding and rolling friction. The validity of the theory, however, depends so much on the simple assumption that the repulsion has a much greater rate of change and a smaller range of action than the attraction, that we shall attempt to show in a simple way how the same hypothesis is consistent with the ordinary phenomena of elasticity. A number of writers have dealt mathematically with the connexion between elasticity and atomic forces, but a

rigorous treatment of the subject is hardly possible with our present limited knowledge of the behaviour of neighbouring atoms in a solid, and we shall therefore only attempt to consider elasticity in an elementary way that seems adequate for the purpose in view.

The characteristic stability of a solid is almost certainly due to the powerful cohesive attraction exerted by the neighbouring atoms acting in equilibrium with an equal and opposite repulsion. Since it is known that each force is some rapidly decreasing inverse function of the distance between the atoms, how does a solid support and recover from a large stress, if its atoms are just in equilibrium under no stress, and an applied tension actually draws them apart and so reduces the cohesive bond? If the attraction and repulsion have characteristics, such as are shown in fig. 1, the tenacity and elasticity of a material can be explained. The point P corresponds to a state of no stress with the atoms under equal repulsive and attractive forces. As a tension is applied causing an external force F to come into action on the atom, the atoms separate slightly and both A and R are diminished, but R to a considerably greater extent than A. The rate of change of the *repulsion* is the main factor in determining the elasticity, the variation in the force of attraction being relatively small within the range of elastic strain. The dotted curve in fig. 1 represents the value of A−R which is equal to the applied force F. As the tension increases, a point is reached at which A−R has a maximum value; at this point the atoms will separate with further increase in tension. By our hypothesis the displacement of the atoms at this point is small compared with the field of attraction, and the maximum value of A−R is not much less than PJ, the normal cohesion under no stress. Hence the tenacity is almost entirely determined by the cohesive attraction, whereas the elastic modulus is similarly determined by the value of $\frac{dR}{dx}$, the attraction being a comparatively flexible bond.

When a compressive stress is applied, the atoms are forced nearer together and we pass upwards along both the curves. The initial rate of change of R will be the same as before, and therefore the same modulus of elasticity would be expected, which is found by experiment to be the case. Under compression no limiting value of A−R is indicated as in tension, and if there is a limit to the amount of uniform compression a solid can withstand, it cannot be realized

experimentally. The hypothetical forces thus lead generally to a natural explanation of the elastic behaviour of a solid.

It can be shown more quantitatively from the known data of elasticity that the repulsion field must have a considerably higher gradient and smaller range than the attraction.

Consider any two neighbouring atoms in a body which is subjected to a uniform compression, and let the external pressure p give rise to a force F thrusting the atoms closer together. If the distance between the atoms is e, and an increment dF in the force produces a decrement de in this distance, we must have

$$d\mathrm{F} = d\mathrm{R} - d\mathrm{A}$$

or

$$\frac{d\mathrm{F}}{de} = \frac{d\mathrm{R}}{de} - \frac{d\mathrm{A}}{de}.$$

Now, $\frac{d\mathrm{R}}{de}$ and $\frac{d\mathrm{A}}{de}$ are both necessarily negative, and $\frac{d\mathrm{F}}{de}$ is also negative; hence $\frac{d\mathrm{R}}{de}$ must exceed $\frac{d\mathrm{A}}{de}$ for stable equilibrium to exist.

Let it be assumed that the attraction is in the neighbourhood of the point P of fig. 1 can be represented by the simple inverse relation

$$\mathrm{A} = \frac{\mathrm{B}}{e^n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

without assuming any value for the exponent n.

Then

$$\frac{d\mathrm{A}}{de} = -\frac{n\mathrm{B}}{e^{n+1}} = -\frac{n\mathrm{A}}{e}. \quad . \quad . \quad . \quad . \quad (23)$$

If K is the modulus of compressibility,

$$dp = -3\mathrm{K}\frac{de}{e};$$

and also $\mathrm{F} = \beta e^2 p$, where β is a factor not greatly different from unity and dependent on the type of atomic packing.

Hence

$$d\mathrm{F} = -3\mathrm{K}\beta e\, de$$

or

$$\frac{d\mathrm{F}}{de} = -3\mathrm{K}\beta e. \quad . \quad . \quad . \quad . \quad . \quad (24)$$

We can also write $\mathrm{A} = \beta e^2 f$, where f is a stress which corresponds to the limiting cohesion between the atoms.

This stress f represents the ideal tenacity or the tenacity under a state of triple tension.

Hence $$\frac{d\mathrm{A}}{de} = -\frac{n\mathrm{A}}{e} = -\beta nef.$$

So that $$\frac{d\mathrm{F}}{de} = \frac{3\mathrm{K}}{nf}\frac{d\mathrm{A}}{de}$$

and $$\frac{d\mathrm{R}}{de} = \frac{d\mathrm{F}}{de} + \frac{d\mathrm{A}}{de} = \left(\frac{3\mathrm{K}}{nf} + 1\right) \times \frac{d\mathrm{A}}{de}. \quad . \quad . \quad (25)$$

Considering the quantity within brackets, although there is much uncertainty as to the value of the ideal tenacity f, there is little doubt that this is a stress considerably smaller than the modulus K. As regards the exponent n, there is again a lack of definite knowledge, but values 2 or 4 are frequently suggested. For our present purpose we may at least regard n as not greatly different from 3, so that we can conclude from equation (26) that the elastic properties of matter qualitatively support our assumption that $\frac{d\mathrm{R}}{de}$ considerably exceeds $\frac{d\mathrm{A}}{de}$, even if they yield no very definite numerical information as to the ratio of the two force gradients.

That the total range of the repulsion force is small compared with the range of the attraction is also supported by another physical property of solids. It is well known that the total dilatation of a solid from absolute zero to its melting-point is approximately constant for nearly all substances, and amounts to about 0·02 in linear dimensions. Thus the complete range of the solid state corresponds to an expansion of the atomic lattice of only about 2 per cent., beyond which the solid condition of equilibrium vanishes. This quantity, in terms of our hypothesis, must be associated with the effective range of the repulsion. The attraction between atoms, on the other hand, is known to extend for a distance at least exceeding the distance between the atoms.

The author wishes to express his thanks to Sir J. E. Petavel and Mr. J. E. Sears for their continued interest and encouragement, and also to Sir T. E. Stanton and Sir W. B. Hardy for kindly reading and criticizing his first investigation into a subject which owes so much of its advance to them.

CVII. *The Size of the Molecules of Fatty Acids.* *By* F. J. Hill, *B.Sc., Research Student at the University College of the South-West of England, Exeter* *.

1. *Introduction.*

THE effect on the surface tension of the addition of small quantities of oil to water has been widely studied. The experiments of Devaux †, Rayleigh ‡, Marcelin §, and Miss Pockels ‖ show that very thin oil films do not alter appreciably the surface tension, but that the tension suddenly begins to decrease when a certain critical layer of oil is placed upon the water surface. With thicker films the value approaches the surface tension of the pure oil. It is assumed that the amount of oil necessary to give the critical point at which the surface tension changes corresponds to a layer of thickness one molecule. This assumption is now generally accepted and has been confirmed by X-ray analysis. Langmuir ¶ has applied it in his work on the orientation of molecules of substances floating on water, and great advances have thus been made in the subject of molecular structure. He used a balance method to measure the excess pull exerted on a paper strip placed in the surface and separating a pure water surface from one contaminated by a known thickness of oil This subject has been continued with considerable success by Adam, who used an apparatus very similar to Langmuir's.

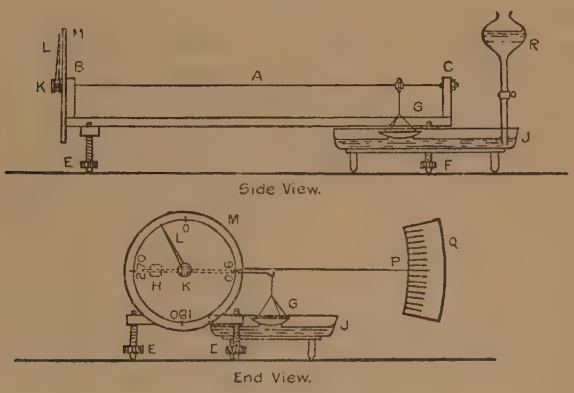
The present work describes experiments made to determine similar quantities with different apparatus. The method of obtaining the critical thickness differs a little from Langmuir's, but the calculation of results follows the same process.

The actual method employed to measure the surface tension was one combining du Nouy's "tensiometer" and Ferguson's sphere method. The apparatus designed consisted essentially of a long fine steel wire A about a metre long stretched between the two uprights B, C of a stand made of brass bars supported on levelling screws E, F.

* Communicated by Prof. F. H. Newman, D.Sc., A.R.C.S., F.Inst.P.
† Devaux, Rep. of Smithsonian Inst. 1913, p. 261.
‡ Lord Rayleigh, Phil. Mag. [5] xlviii. p. 331 (1899).
§ A. Marcelin, *Ann. d. Phys.* [9] i. p. 19 (1914).
‖ A. Pockels, 'Nature,' xliii. p. 437 (1891).
¶ Langmuir, J. A. C. S. xxxix. p. 1848 (1917); Proc. Nat. Acad. Sci. iii. p. 251 (1917).

One end of the wire was soldered into a large screw which was fixed in the pillar C. The surface tension could then be calculated from the pull exerted on the surface of a large evaporating dish suspended from a brass arm, the latter being fixed by means of grub screws on the wire near the end C. A brass cylinder H which could be screwed along the other arm served as a counterpoise for G, and the liquid was contained in a large flat dish J. The surface of G was raised or lowered by applying a torque to the wire A by means of the brass head K fixed to the other end of the wire. The torsion was measured by the travel of the pointer L over the circular scale of degrees marked on the brass plate M.

Fig. 1.



2. *Experiments.*

This arrangement is easy to set up, and it was found to be very sensitive, all the quantities to be measured having comparatively large values. Thus the degree of accuracy was fairly high. Although the actual values of the surface tension were not required in this work, a calibration was first made by noting the twist corresponding to a given weight placed on the evaporating dish, the latter serving as a scale-pan. In this way a linear relationship between scale reading and weight was observed. The equation used to convert scale readings into absolute force measure was that derived by Ferguson * for the raising of a sphere from a liquid surface, viz. :

$$m = 4\pi\rho a^2 \left\{ R - \sqrt{\frac{aR}{3}} - \frac{a}{3} \right\}, \quad . \quad . \quad . \quad (1)$$

* A. Ferguson, Phil. Mag. xxvi. p. 925 (1913).

where m is the surface tension pull, ρ the density of the liquid, $a^2\left(\equiv\frac{T}{g\rho}\right)$ the capillary constant, and R the radius of the spherical surface.

The head K was first turned so that the beam was horizontal and the pointer L exactly at the zero mark. It was arranged that the beam always returned to this zero position at every reading of the torsion made. To obtain this zero setting a long glass pointer, drawn out very fine, was attached by wax to the beam, and it moved over a reference scale Q. The actual setting was made by viewing the end of the glass pointer with a microscope set initially with the cross-wire on the image of the pointer when the latter was in the zero position.

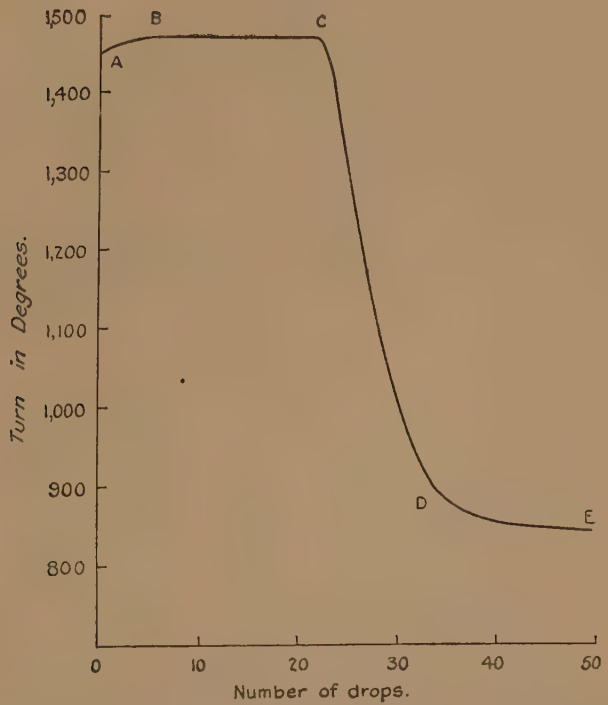
Water was then poured into the flat dish, and to make the final adjustment the water was slowly run in from the funnel R until it just touched the surface of the dish G. The latter at this point was suddenly depressed. The pointer P was then restored to the zero position by turning the head K and the reading, given by L, noted when the image of the pointer came just on the cross-wire of the microscope. This setting could be made to within one degree, giving an accuracy of 1 in 1000.

The torque corresponding to the tension of an oily water-surface was then found. A small quantity of fatty acid—the acids actually used were oleic acid, palmitic acid, and stearic acid—was weighed and dissolved in about 100 c.c of ether. This dilute solution was allowed to fall on the water surface, the quantity being controlled by dropping the solution from a tube provided with a control tap. Five or ten drops were run out, the ether allowed to evaporate, and the twist required to bring the pointer back again to zero observed ; a few more drops were added and the process repeated. It was necessary before adding drops of solution to rotate the wire so that the beam was lowered because the addition of the ether causes a sudden lowering of surface tension as it spreads, and thus otherwise the wire would be in a state of tension greater than that necessary to suspend the dish G. The latter would then detach itself from the surface.

Using the series of readings, a graph was constructed—number of drops against number of degrees of turn. The general form of the curve is shown in fig. 2. A corresponds to pure water. Along ABC the quantity of acid on the surface is not sufficient to affect the surface tension. It appears that the slight rise A to B sometimes obtained

is produced by the first portion of the ether tending to clean the surface and to drive away impurities to the edges. At C the tension decreases more or less sharply until D is reached, after which the curve becomes asymptotic to the axis of quantity of liquid at E. Thus C gives the point where there is just sufficient acid to cover the surface in an unimolecular layer. At E the value of the surface tension of the liquid in bulk is approached. The important section

Fig. 2.



of the curve in this work is that around the point C, and it is advantageous to obtain as sharp a turn as possible.

Graphs were drawn for each set of readings, and the number of drops n corresponding to C determined. If the solution consists of m gm. of acid in M gm. of solution and the weight of one drop is w gm., the surface occupied by one molecule of the acid in the plane of the water surface is given by

$$\omega_M = \frac{AWM}{nwm\mathrm{N}}, \quad \ldots \ldots \quad (2)$$

where A is the area of the water surface, W the molecular weight of the acid, and N is Avogadro's number.

The effective thickness of the molecule will then be

$$b_M = \sqrt{\omega_M}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The thickness of the film, *i. e.* the length of the molecule, l_M is given from

$$l_M = \frac{nwm}{MAs}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where s is the specific gravity of the acid.

It will be noted that the following assumptions are made:—

(i.) The value of the surface-tension changes from that of pure water when the oil film becomes unimolecular in thickness ; with quantities of liquid less than this there is no alteration of the surface tension of water.

(ii.) The density of the substance in molecular form is the same as that of the substance in bulk. There is a considerable mass of evidence in support of this assumption.

3. *Experimental Results and Discussion.*

Calibration :—

Radius of spherical surface	6·762 cm.
Turn for 6 gm.	1489°
Surface tension for 1489°	74·9 dynes/cm.
Avogadro's constant	$N = 607 \times 10^{21}$
Area of water surface	A = 604 sq. cm.

(i.) Oleic acid, $C_{18}H_{32}O_2$.

Molecular weight	W = 282
Specific gravity	s = ·808 gm./c.c.

No. of Expt.	Weight of acid, m gm.	Weight of solution, M gm.	Weight per drop, w gm.	Number of drops, n.	ω_M $\times 10^{16}$, sq. cm.	b_M $\times 10^8$, cm.	l_M $\times 10^8$, cm.
1.....	·02317	71·8	·01473	10·9	54	7·4	10·7
2.....	·02317	71·8	·01608	10·0	54	7·4	10·6
3.....	·0140	73·95	·01621	18·4	50	7·1	11·6
11.....	·0247	34·20	·003082	21·0	61	7·8	9·4
14.....	·0247	34·20	·005003	14·0	55	7·4	10·3
17.....	·0247	34·20	·002963	24·0	55	7·4	10·5
			Mean values		54·8	7·4	10·5

(ii.) Palmitic acid, $C_{16}H_{32}O_2$.

Molecular weight ..... W=256
Specific gravity ..... s=·853 gm./c.c.

No. of Expt.	Weight of acid, m gm.	Weight of solution, M gm.	Weight per drop, w gm.	Number of drops, n.	$\omega_M \times 10^{16}$, sq. cm.	$b_M \times 10^8$, cm.	$l_M \times 10^8$, cm.
3.....	·0158	71·82	·01668	24·6	28	5·2	17·1
5.....	·0158	71·82	·01649	20·5	35	5·9	15·3
7.....	·0158	71·82	·01536	21·8	35	5·9	15·2
12.....	·0132	32·173	·003055	44·7	36	6·0	13·9
15.....	·0132	32·173	·004656	30·4	44	6·6	11·3
18.....	·0132	32·173	·003035	48·0	43	6·5	11·6
			Mean values		36·8	6·0	14·1

(iii.) Stearic acid, $C_{18}H_{36}O_2$:

Molecular weight ..... W=284
Specific gravity ..... s=1·00 gm./c.c.

No. of Expt.	Weight of acid, m gm.	Weight of solution, M gm.	Weight per drop, w gm.	Number of drops, n	$\omega_M \times 10^{16}$, sq. cm.	$b_M \times 10^8$, cm.	$l_M \times 10^8$, cm.
4.....	·0161	73·116	·016537	24·2	32	5·6	14·6
6.....	·0161	73·116	·016223	24·6	32	5·6	14·6
9.....	·0080	73·966	·015448	50·2	34	5·8	13·9
13.....	·0147	36·937	·0031176	77·8	29	5·4	16·0
16.....	·0147	36·937	·004894	52·9	27	5·2	17·1
19.....	·0147	36·937	·003144	80·3	29	5·4	16·6
			Mean values		30·5	5·5	15·5

The mean results obtained by this method are as follows:—

Oleic acid	54·8	7·4	10·5
Palmitic acid	36·8	6·0	14·1
Stearic acid	30·5	5·5	15·5

whereas Langmuir by his method finds the following :—

Oleic acid	46	6·8	11·2
Palmitic acid	21	4·6	24
Stearic acid	22	4·7	25

It may be seen that, although the results agree fairly well with Langmuir's in some cases, there are discrepancies

between the values for palmitic acid and stearic acid. Thus in the present work the ratio length/breadth is respectively 1·4, 2·3, and 2·8, but he obtains 1·6, 5·2, and 5·3 respectively. Among the six results for each acid the values for oleic acid and stearic acid are quite consistent, but rather wide variations occur in the case of palmitic acid.

The sensitivity of the experiment depends upon the degree of accuracy with which the turning-point of the curve may be evaluated. It is advisable to construct a graph with a run of drops, say with the addition of five for each reading, and then repeat the experiment, concentrating on readings a little greater and less than those at the turning-point, proceeding by adding one drop only each time. The other quantities are either known accurately by independent methods (as, for example, the molecular weight or the specific gravity), or may be determined with some degree of accuracy, *e.g.*, the twist of the wire.

The degree of definition of the critical turning-point may be increased by arranging that a larger number of drops shall be used, that is, very dilute solutions may be employed. The apparatus employed possesses distinct advantages. Readings may be easily and quickly taken. The torsional motion is gradual and steady, and settings may be made to an accuracy of 1 in 1000. Experiments involving placing weights in a scale-pan to measure the pull lead to a jerky action, with consequent oscillation of the pulling surface. For simplicity of action the torsion method surpasses the balance method. The same apparatus may be modified for use with an expanding or contracting film such as Langmuir used, instead of the boundaries being fixed and more acid being introduced as described in the present work.

The writer is gratefully indebted to Dr. F. H. Newman for his helpful suggestion and criticism in this work.

CVIII. *Note on a Geometrical Radiation Theorem.*

By C. E. Wright *.

1. RECENT papers in this Journal dealing with the question of the illumination of a surface by radiation transmitted through an aperture suggest that the following treatment of some particular cases may be of interest.

* Communicated by the Author.

Some reductions of the general integral to cases of double integration only are discussed in most text books on geometrical optics ; for the cases to be considered in this note more special methods will suffice, and are perhaps easier of application.

2. An area situated in a plane transmits uniform intensity I per unit area. The illumination of a second area in a parallel plane, the distance between the planes being l, is to be considered. A straight line perpendicular to the planes meets them in points O, O_1, origins of parallel sets of rectangular axes (Ox, Oy), (O_1x',O_1y'). The general expression for intensity becomes

$$Il^2 \iiiint \frac{dx\,dy\,dx'\,dy'}{\{(x-x')^2+(y-y')^2+l^2\}^2}. \quad . \quad . \quad (1)$$

The case to be considered deals with similarly oriented rectangles (with sides parallel to the axes) in the two planes. The limits for the integrations are then constants, and from this the following simplification is derived. Since x and $-x'$ are similarly involved, let $x-x'=u$. For the integration with respect to x, $du=dx$; on substitution of constant limits (as x_1) the substitution $x_1-x'=u$, $-dx'=du$ reduces the integration $\iint dx\,dx'$ to $-\iint(du)^2$. Similarly for y and y'.

Write $x-x'=u$, $y-y'=v$, expression (1) becomes

$$Il^2 \iiiint \frac{(du)^2\,(dv)^2}{(u^2+v^2+l^2)^2}.$$

Degenerate cases occur involving fewer integrations. Hence it is desirable to obtain the results of the successive integrations, which are as follow :—

$$Il^2 \iiiint \frac{(du)^2(dv)^2}{(u^2+v^2+l^2)^2}$$

$$= \tfrac{1}{2}Il^2 \iiint \frac{du(dv)^2}{(v^2+l^2)^2}\left\{\tan^{-1}\frac{u}{(v^2+l^2)^{\frac{1}{2}}}+\frac{u(v^2+l^2)^{\frac{1}{2}}}{u^2+v^2+l^2}\right\}. \quad (a)$$

$$= \tfrac{1}{2}Il^2 \iint \frac{(dv)^2}{(v^2+l^2)^{\frac{3}{2}}}\,u.\tan^{-1}\frac{u}{(v^2+l^2)^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

$$= \tfrac{1}{2}I \int dv \left\{ \frac{uv}{(v^2+l^2)^{\frac{1}{2}}}\tan^{-1}\frac{u}{(v^2+l^2)^{\frac{1}{2}}} + l\tan^{-1}\frac{l}{v} \right.$$

$$\left. -(l^2+u^2)^{\frac{1}{2}}\tan^{-1}\frac{(l^2+u^2)^{\frac{1}{2}}}{v}\right\} \quad . \quad . \quad . \quad . \quad (c)$$

$$= \tfrac{1}{2}\mathrm{I}\Big[u(v^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{u}{(v^2+l^2)^{\frac{1}{2}}} - \tfrac{1}{2}l^2\log(u^2+v^2+l^2)$$
$$+ lv\tan^{-1}\frac{l}{v} + \tfrac{1}{2}l^2\log(v^2+l^2) - (l^2+u^2)^{\frac{1}{2}}v\tan^{-1}\frac{(l^2+u^2)^{\frac{1}{2}}}{v}\Big], \quad \ldots \quad (d)$$

and to complete the necessary list,

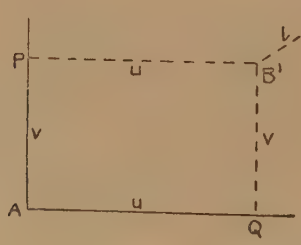
$$\mathrm{I}l^2\iint\frac{du\,dv}{(u^2+v^2+l^2)^2}$$
$$= \tfrac{1}{2}\mathrm{I}\Big[\frac{v}{(v^2+l^2)^{\frac{1}{2}}}\tan^{-1}\frac{u}{(v^2+l^2)^{\frac{1}{2}}} - \frac{u}{(u^2+l^2)^{\frac{1}{2}}}\tan^{-1}\frac{v}{(u^2+l^2)^{\frac{1}{2}}}\Big]. \quad \ldots \quad (e)$$

3. Since the limits are constants, functions of v (or u) only may be omitted in (d); it is also convenient to write

$$\tan^{-1}\frac{(l^2+u^2)^{\frac{1}{2}}}{v} = \tfrac{1}{2}\pi - \tan^{-1}\frac{v}{(u^2+l^2)^{\frac{1}{2}}},$$

and the integral then reduces to the form

$$\tfrac{1}{2}\mathrm{I}\Big[u(v^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{v}{(v^2+l^2)^{\frac{1}{2}}} + v(u^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{v}{(u^2+l^2)^{\frac{1}{2}}}$$
$$- \tfrac{1}{2}\pi v(l^2+u^2)^{\frac{1}{2}} - \tfrac{1}{2}l^2\log(u^2+v^2+l^2)\Big]. \quad (f)$$



Let A be any corner of one rectangle, B any corner of the second, B′ the projection of B on the plane of the first, B′P, B′Q, AP, AQ parallels to the axes as shown. The integral is

$$\sum_{A}\sum_{B}\pm\,.\{B'Q\,.\,BP\,.\,\angle ABP + B'P\,.\,BQ\,.\,\angle ABQ$$
$$- \tfrac{1}{2}\pi B'P\,.\,BQ - l^2\log AB\},$$

with proper assignation of the signs.

Even with this reduction, the insertion of general limits leads to complicated expressions. The physical interpre-

tation gives, however, a curious analytical result when the planes of the two rectangles coincide ; for

$$\underset{l\to 0}{\text{Limit}}\ \mathrm{I}l^2\iint\frac{(du)^2(dv)^2}{(u^2+v^2+l^2)^2}=\pi\mathrm{I}$$

$\times$ area common to the two rectangles.

The similar theorem is deduced for two concentric circles (Prof. E. A. Milne, Phil. Mag. [7] vii. p. 275, Feb. 1929), and is readily deduced for concentric squares from results set out below. Hence for rectangles

$$x=a \text{ to } b,\quad y=c \text{ to } d,\quad x'=e \text{ to } f,\quad y'=g \text{ to } h,$$

the value of

$$\underset{l\to 0}{\text{Limit}}\int_a^b dx\int_c^d dy\int_e^f dx'\int_g^h dy'\{(x-x')^2+(y-y')^2+l^2\}^{-2}$$

$$(a<b,\ \ c<d,\ \ e<f,\ \ g<h),$$

considered as a function of e, f, g, h, $=\pi\mathrm{I}(b-a)(d-c)$ if $e<a<b<f$, $g<c<d<h$ is zero if $(a, b)\lessgtr(e, f)$, $(c, d)\lessgtr(g, h)$, whilst if e or f lies between a and b, and g or h lies between c and d, the integral is linear in the variable or variables which occur in the statements of inequality.

These results cannot readily be obtained from the form of the integrand ; in fact effective elements of the integral arise, in the limit, for zero values of both u and v, whence expansion of the integrand in ascending powers of l is impossible.

4. The results for coaxial squares (with parallel sides of lengths $(2a, 2b)$) admit of reduction. In the form § 3 (f), the first two terms now contribute equal amounts, the third term gives zero. The final result may be written

$$\mathrm{V}=4\mathrm{I}\Big\{p(p^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{p}{(p^2+l^2)^{\frac{1}{2}}}-p(q^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{p}{(q^2+l^2)^{\frac{1}{2}}}$$

$$+q(q^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{q}{(q^2+l^2)^{\frac{1}{2}}}-q(p^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{q}{(p^2+l^2)^{\frac{1}{2}}}$$

$$-\tfrac{1}{4}l^2\log\frac{(2p^2+l^2)(2q^2+l^2)}{(p^2+q^2+l^2)^2}\Big\},$$

with $p=a+b$, $q=a-b$.

For equal squares, $p=2a$, $q=0$ gives

$$4\mathrm{I}\Big[2a(4a^2+l^2)^{\frac{1}{2}}\tan^{-1}\frac{2a}{(4a^2+l^2)^{\frac{1}{2}}}-2al\tan^{-1}\frac{2a}{l}$$

$$-\tfrac{1}{4}l^2\log\frac{l^2(8a^2+l^2)}{(4a^2+l^2)^2}\Big].$$

If in this $l=2a\xi$, $V/16a^2I=\eta$, the relation between ξ and η is given by

$$\eta=(1+\xi^2)^{\frac{1}{2}}\tan^{-1}\frac{1}{(1+\xi^2)^{\frac{1}{2}}}-\xi\tan^{-1}\frac{1}{\xi}-\tfrac{1}{4}\xi^2\log\left\{1-\frac{1}{(\xi^2+1)^2}\right\}.$$

From this, or from the previous form, the known limiting cases when $l\to 0$ or $l\to\infty$ may be obtained. Between $\xi=0$ and $\xi=\infty$, η continually decreases.

The special case treated by Dr. L. F. Richardson (Phil. Mag. [7] vi. p. 1019, Nov. 1928) requires $\xi=1$, giving

$$V=Il^2\left[4\sqrt{2}\tan^{-1}\frac{1}{\sqrt{2}}-\pi+\log\frac{4}{3}\right]=0{\cdot}6278Il^2.$$

5. Let the results (*a*), (*b*), (*c*) of § 2 be written

$$\iiint du(dv)^2\,.\,\phi_1,\quad \iint(dv)^2\,.\,\phi_2,\quad \int dv\,.\,\phi_3 \quad \text{respectively,}$$

and let $u=x-x'$, $v=y-y'$, unless otherwise stated. The following cases are now deducible.

In ϕ_1 write $y=c$, and take the result between limits $x=-a$ to $+a$. On multiplication by α, the result gives the intensity of illumination at $(x',\ y')$ due to a slit of breadth α extending from $x=-a$ to $+a$ along the line $y=c$.

Multiply $-\phi_2$ by $\alpha\beta$, write $y=c$, $y'=c'$, and take the result between limits $x=-a$ to $+a$, $x'=f$ to g. The result is the illumination on a slit situated on $y'=c$, of breadth β and extending from $x'=f$ to $x'=g$, due to an illuminating slit of breadth α and length $2a$ placed along the line $y=c$.

ϕ_3 with change of sign similarly gives the illumination, due to a rectangle in one plane, of a slit in the other plane parallel to one edge of the rectangle.

Finally, (*e*) may be interpreted so as to give the illumination on a straight slit due to a perpendicular slit in the parallel plane *.

6. The above method admits of application to other problems of a physical nature. Some of these applications will, it is hoped, be dealt with in a future note.

Blackheath.
March 11, 1929.

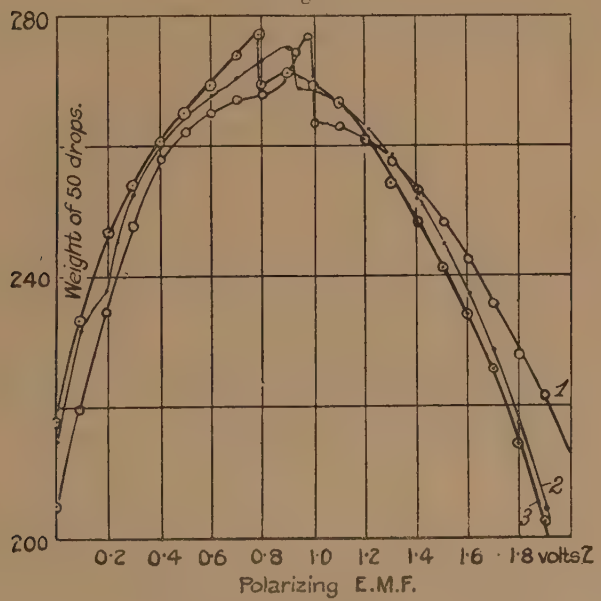
* The intensity of illumination at any point in space due to illumination by a rectangle can also be derived from (*e*).

CIX. *Electrolysis with a Mercury Cathode.*—Part II. *Explanation of the Anomalies on the Electro-capillary Curves.* *By* Jaroslav Heyrovský, *D.Sc., Ph.D., Professor in Physical Chemistry, and* Rudolph Šimůnek, *Ph.D., Assistant in Experimental Physics, Charles' University, Prague* *.

Introduction.

As mentioned in Part I. of the above communication [1], we owe to Prof. B. Kučera the introduction of the drop-weight method for the determination of the interfacial

Fig. 1.



(1) $n/1000$ H_2SO_4. (2) $n/500$ Na_2SO_4.
(3) $n/100$ K_2SO_4.

tension of polarized mercury. However, the electro-capillary curves thus obtained often differ considerably from those obtained by Lippmann's classical method by means of the capillary electrometer. In some solutions Kučera's curves deviate from the ordinary electro-capillary parabolas by exhibiting a marked anomalous maximum of interfacial tension (see fig. 1), which at a certain polarizing E.M.F.

* Communicated by the Authors.

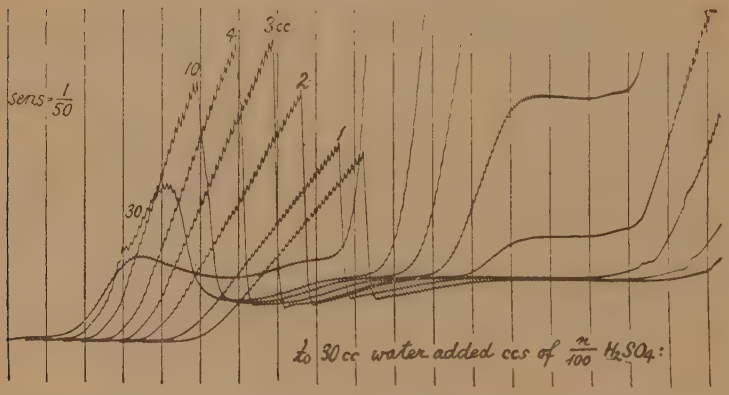
abruptly falls to coincide again with the regular course of the parabola.

Professor B. Kučera himself described the occurrence of these anomalies in two of his communications [2] [3], and suggested to the present authors to investigate the cause of these anomalies from the physico-chemical standpoint. A preliminary report of these investigations has been published in the *Bulletin International de l'Académie des Sciences de Bohême*, 1927, presented October 21st. In the following these anomalous maxima of interfacial tension will be called Kučera's anomalies.

Experimental.

The measurements were first carried out as described by Prof. Kučera by keeping the electrolyte solution in a beaker

Fig. 2.



open to the air. A layer of mercury at the bottom of this beaker served as anode and the mercury drops falling slowly from a thick-walled glass capillary as cathode. The polarization was effected by connecting these electrodes to the terminals of a resistance-box potentiometer adjusted so that 1 millivolt of the E.M.F. corresponded to 1 ohm in the box (compare Part I. p. 305, fig. 2). The source of the E.M.F. was a 2- or 4-volt accumulator. Aqueous solutions of sulphuric acid and sodium and potassium sulphate in various dilutions were used as electrolytes, some 60 solutions having been thus investigated.

To find the region of concentrations in which Kučera's anomalies are most prominent, the concentrations were

varied from normal by two-fold dilutions down to $n/10000$. In all dilute solutions the anomalous effect looked for was noticeable, and most marked in concentrations from $n/500$ to $n/1000$. It was further ascertained that the maxima occurred whether slowly- or quickly-dropping capillaries were used, or ordinary or extraordinary purity of reagents and distilled water were employed. The character of this anomaly remained the same no matter whether freshly-prepared solutions were used or old ones long standing with mercury. The suggestion of Prof. Kučera that this secondary maximum may be due to traces of mercury coming into solution by oxidation on contact with air was carefully investigated by Dr. Rasch [4], who found that this explanation cannot hold: addition of mercuric oxide or mercurous salts to the solution caused only unimportant changes at the beginning of the electro-capillary curves, and no difference in the anomaly was found whether anions forming insoluble salts with mercury (*e.g.*, chlorides, hydroxides, iodides) or soluble ones (nitrates) were present in the solution *.

The influence of the increase or decrease of the applied E.M.F. upon the potential at which the discontinuous fall of the interfacial tension occurred was closely investigated in the case of $n/1000$ sulphuric acid. No marked difference could be detected whether we approached the maximum from higher or lower voltages, it always occurred at 0·96 volt of polarization. The same solution as standing in a beaker open to the air has now been investigated polarographically, which method elucidated at once the nature of the Kučera anomaly.

Concerning this method little will be mentioned here, since it has been fully described recently in numerous communications [5]. The method consists in the investigation of current-voltage polarization curves, now registered automatically by means of a special photo-registering apparatus, the polarograph †. The polarizing voltage is plotted as abscissa against the corresponding current, the curve being drawn on a rotated photographic paper by a beam of light reflected from the mirror of a sensitive galvanometer.

* For the entirely different type of polarization curves with solutions containing mercury salts, see the recent paper of P. Herasymenko, J. Heyrovský, and K. Tančakivský, "Maxima on Current-Voltage Curves.—Part III. The Electrolysis of Mercury Salts Solutions with Dropping and Steady Mercury Cathodes." Trans. Faraday Soc. xxv. p. 152 (1929).

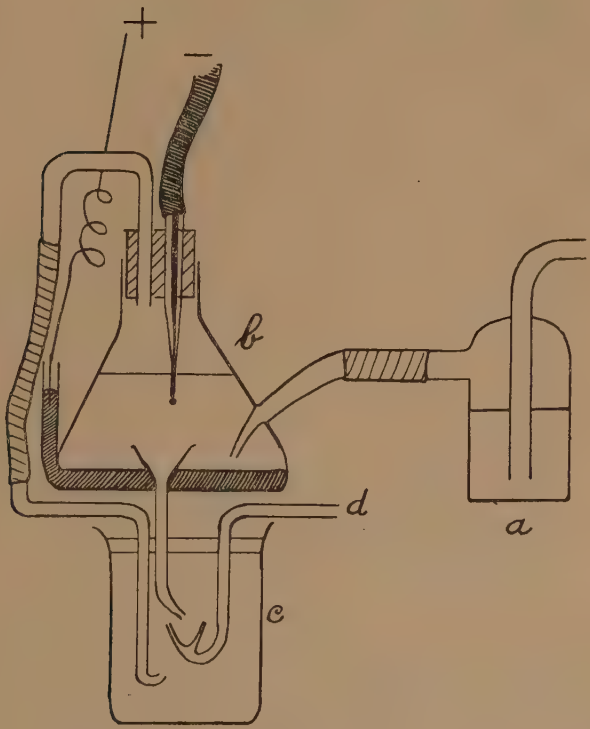
† The apparatus used lately was constructed by the firm, Dr. V. Nejedlý, Prague, Radešovice, No. 92.

Qualitative and quantitative deductions are made from the increase of current occurring at various potentials about reducible matters dissolved in the electrolyte solution. Hitherto all solutions to be investigated were carefully freed from air by bubbling hydrogen through them in order to avoid the great increase of current due to the reduction of atmospheric oxygen.

The polarographic curve obtained by electrolysing the $n/1000$ sulphuric acid solution in the same beaker exposed to the air, and using the same capillary of the mercury-dropping cathode with all experimental conditions unchanged, revealed a very sharp maximum (see fig. 2) of the current falling discontinuously at 0·96 volt, *i. e.*, at the same voltage as on the electro-capillary curve. It at once became evident that this polarographic maximum, just as the electro-capillary one, can only be due to the atmospheric oxygen dissolved in the solution. The increase of current on air shows by its magnitude (after the maximum) that the reducible matter is present in a concentration of ca. 0·0012 gram equivalent per litre, which corresponds to the concentration of atmospheric oxygen dissolved in aqueous solutions at room temperature. Further, the increase of current starting from the beginning of polarization proves that the matter in solution is an easily reducible substance. To demonstrate this action of oxygen beyond doubt, the oxygen content in solutions was changed, its partial pressure being varied from zero to one atmosphere. In all cases the electro-capillary and polarographic curves were determined. The special electrolytic vessel used in this investigation is shown in fig. 3. In this arrangement first pure hydrogen was passed through the solution of a dilute electrolyte ($n/1000$ H_2SO_4 or $n/100$ KCl) contained in the wash-bottle *a*, electrolysing vessel *b*, and the beaker *c*, in which it was covered by a layer of paraffin-oil. After four hours' bubbling the current of hydrogen was stopped and the electro-capillary parabola obtained by collecting the polarized mercury drops in the glass spoon *d* and weighing. In this way Kučera's method could be applied without the intervention of the atmospheric oxygen. The resulting curve was a smooth parabola (see fig. 4), No. 1, devoid of any anomalies. Next, the same solution was investigated polarographically under exactly identical conditions of polarization. The horizontal line thus registered (see fig. 5) showed that in this solution no trace of reducible matter is contained. Next, oxygen (from a cylinder) was passed through the solution for several hours, and both the polarographic as well as the electro-capillary

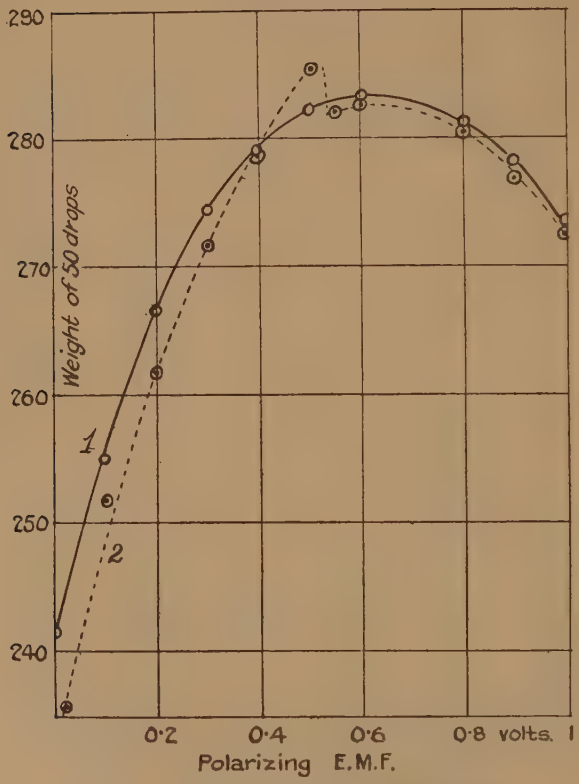
curves were obtained ; the polarogram showed a curve similar to that of No. 4 (fig. 6), which exhibited a marked maximum and a residual current almost five times as great as observable on the curve belonging to the solution standing open on air (compare fig. 6, curve 3). The electro-capillary parabola was much deformed, showing a prominent secondary maximum with a discontinuous fall, much more marked

Fig. 3.



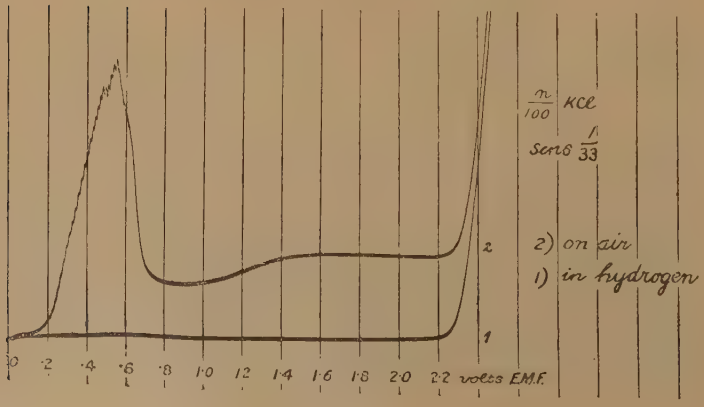
than when obtained with air. The position of the discontinuous fall of the electro-capillary parabola occurring in this solution at 1·34 volt coincided exactly with the voltage of the discontinuous fall on the polarographic curve. From these and similar investigations it became evident that the sudden change of current at the maximum is always accompanied by a sudden change of the interfacial tension of mercury, *i.e.*, by Kučera's anomaly. In view of the

Fig. 4.



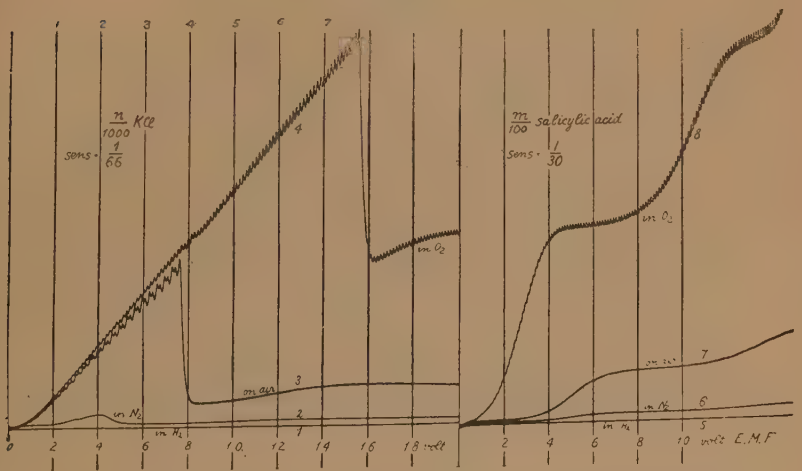
(1) $n/100$ KCl in the atmosphere of hydrogen.
(2) Open to air.

Fig. 5.



experimental difficulties and the slow procedure of the drop-weight method, further investigations on the nature of the anomalies were carried out by the polarographic method only, the parallelism between the two phenomena being taken as certain. Thus one curve could be obtained in 10 minutes polarographically, *i. e.*, automatically, whereas the electro-capillary method required 4 hours of tedious counting of drops and weighing before these results could be plotted on the curve. Moreover, the disturbing influences are much more pronounced on the current-voltage curve than on the electro-capillary one, and the electrolytic changes, which are no doubt here displayed, are far more

Fig. 6.



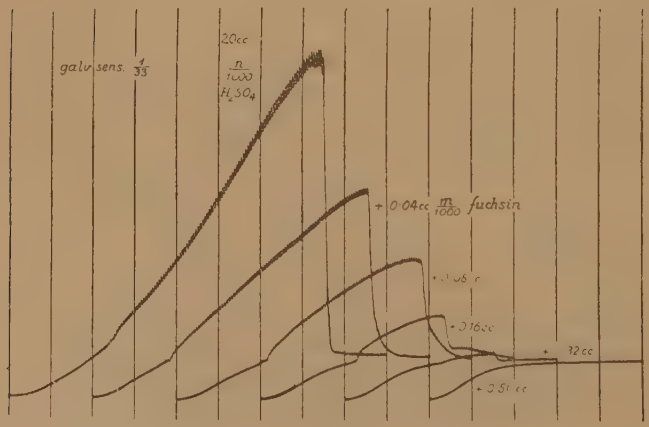
precisely defined by the intensity of current than by the drop-weight method.

Thus, to find polarographically in which concentration the anomaly is most prominent, a series of measurements was made while increasing the concentration of sulphuric acid exposed to air in the electrolytic vessel, *i. e.*, the electrolyte being saturated by the partial pressure of atmospheric oxygen. This polarogram (fig. 2) shows that the highest maximum is reached in a milli-normal solution, which coincides precisely with the previous experience. Much attention is now paid to the conditions of occurrence of the highest maximum by the work of several collaborators (Rasch, Varasová, Dillinger). It has been ascertained that the highest maximum always occurs in a milli-normal

solution of any strong electrolyte. In solutions of weak electrolytes the concentration has to be increased so as to produce an ionic concentration ca. milli-normal; such results, arrived at by Dr. Rasch in this laboratory, coincide again with the facts described by Prof. Kučera in his communication on the appearance of the electro-capillary anomalies in aqueous solutions of fatty acids [3]. Both highest maxima occur here in normalities of $n/10$ to $n/20$, which contain an ionic concentration about milli-normal.

This concentration applies only to the solubility of atmospheric oxygen. If these solutions are saturated by pure oxygen under atmospheric pressure, the electrolyte in which

Fig. 7.



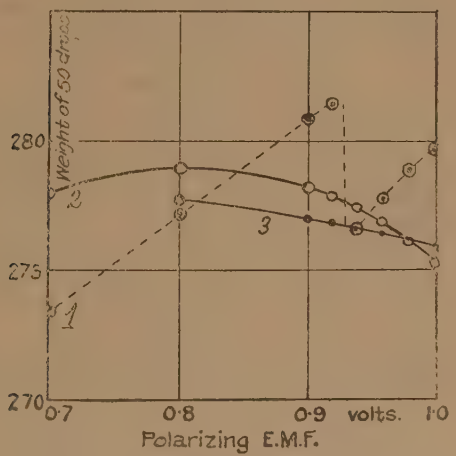
the highest maximum is developed has to be ca. five times millinormal.

Since previous investigations on maxima on polarographic curves have shown the suppressive effect of various electrolytes and non-electrolytes, a similar influence was expected on maxima due to oxygen. The results show that concentrations of strong electrolytes increasing above milli-normal almost equally suppress the maximum (compare Herasymenko, *l.c.*), and that one of the most active matters in this respect, viz. fuchsin (compare Emeljanová and Heyrovský, *l.c.*) was equally powerful in suppressing the maxima due to oxygen. The polarogram (fig. 7) shows this marked effect of fuchsin, where already 1/2 c.c. of a milli-molar solution of fuchsin hydrochloride added to 20 c.c. of a milli-normal sulphuric acid suffice to remove the phenomenon of maximum entirely.

Hence it was concluded that the presence of this substance equally removes Kučera's anomaly; indeed, the electrocapillary curve (fig. 8) obtained with the same fuchsin solution open to air gave a smooth apex of a parabola without the anomaly.

The next experiments were of a quantitative nature to investigate how far the electrolytic current can indicate the content of oxygen in solution. The polarogram (fig. 6) represents the result of this investigation. The lowest horizontal line (curve 1) is the current voltage curve of a milli-molar solution of potassium chloride from which the air

Fig. 8.



$n/1000$ H_2SO_4.

(1) In air. (2) In hydrogen. (3) Air with added fuchsin.

has been driven out by hydrogen. The next curve (No. 2) has been obtained from the same potassium-chloride solution saturated by commercial nitrogen on bubbling through it the gas from a cylinder for several hours. For the third curve the same solution has been standing open to air, whilst for the fourth the solution was saturated by commercial oxygen passing through it from a cylinder. When taking the percentage of oxygen in air as 21 per cent., the saturation currents after the maximum are in relation 0 : 3·5 : 21 : 91, showing the amount of oxygen dissolved in solution from the absorbed gases, viz. pure hydrogen, commercial nitrogen, air, commercial oxygen. An analysis kindly carried out by

Prof. Svěda in the Institute for Analytical Chemistry gives for nitrogen gas in the cylinder 2·83 per cent. and for oxygen gas 93·7 per cent.

Since such quantitative determinations are derived only from the magnitude of the saturation current, the maximum has to be suppressed in order to enable us to compare the total currents. This is easily done by using an aromatic derivative as electrolyte, as, *e.g.*, a centimolar solution of salicylic acid in fig. 6. Curves 5, 6, 8, and 7 were obtained from solutions saturated by the same stream of hydrogen, commercial nitrogen, and oxygen, or standing open to air, just as the curves 1, 2, 4, and 3, their currents increase again in the ratio 0 : 3·5 : 21 : 91, which indicates the oxygen content in the corresponding solutions.

The calculation of the absolute content of oxygen in these solutions has been derived in the following manner :— The magnitude of the saturation current from curve 8 corresponds to 17·5 cm. of the galvanometer deflexion, where the sensitivity was 1/30—that means 525 cm. with the full sensitivity (1 : 1). Now in this arrangement a saturation current causing a deflexion 8 to 10 cm. is due to a concentration of the reducible matter in solution equal to 10^{-4} gr. equiv. per litre. Hence the concentration of the reducible matter present in the solution—in our case commercial oxygen—must be equal to 525/9, *i.e.*, $58 . 10^{-4}$ gr. equiv. per litre, whereas from the curve No. 3 (fig. 6) the saturation current being 2 cm. high with a sensitivity of galvanometer 1/66 leads to a concentration of oxygen almost five times smaller, viz. $14 . 10^{-4}$ gr. equiv. per litre, which corresponds to the solubility of atmospheric oxygen. The exact determination of the solubility of pure oxygen in water under the pressure of one atmosphere at the temperature of 16° C is (according to L. W. Winkler, Landolt-Börnstein tables) 0·04903 gr. per litre, *i.e.*, 0·0061 gr. equiv. Consequently, the solubility of atmospheric oxygen in water, the partial pressure of which is equal to 0·21 atm., is $13 . 10^{-4}$ gr. equiv. These numbers coincide with the above results, a similar agreement being found from saturation currents of any curve provided the concentration of the electrolyte in solution is not great

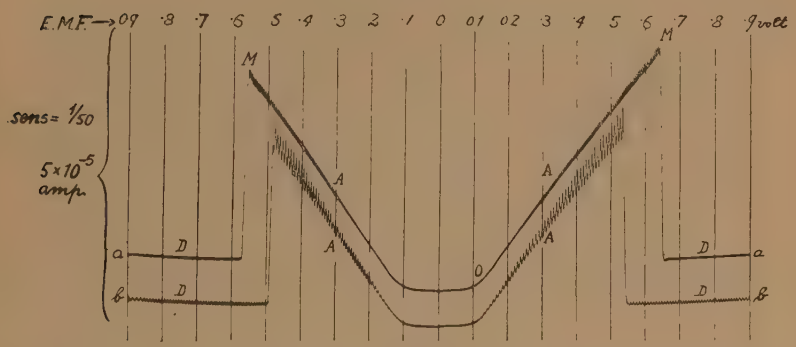
It is interesting to note that on curve 8 the reduction process of oxygen proceeds distinctly in two stages. Special investigations described elsewhere [9] have revealed that the first process consists in reducing oxygen to hydrogen peroxide ; the next is due to the reduction of hydrogen peroxide to water. Each process requires the quantity

of electricity 2 faradays per gram molecule of oxygen so that the total saturation current must correspond to a substance consuming 4 faradays per gram molecule, *i. e.* O_2, as was indeed just calculated.

Discussion of the Results.

The above experiments leave no doubt that it is directly the reduction of oxygen and not of its products in solution which causes the anomalous changes of electro-capillarity in the drop-weight method. It remains to explain the mechanism of this marked discontinuous effect. For this, the explanation of the occurrence of maxima on current-voltage curves has to be put forward as given by one of us

Fig. 9.



recently [8]. It has to be emphasized that such maxima occur in all reduction processes at the dropping mercury cathode whether inorganic or organic matter is deposited or reduced. In all such cases—whether these maxima occur round the potential of the calomel electrode or at a potential as negative as minus 2 volt, when indifferent electrolytes are added—the maxima become more rounded, and finally, with larger additions, suppressed still more so when complex organic compounds, even in mere traces, are present in the solution. No time-effects are observable with the duration of polarization. Further, the backwards polarization from 2 volts to zero gives a curve coinciding with the onwards polarization from zero to 2 volts, which is shown in fig. 9 *. Slight differences will be noted in this polarogram with the

* The slight oscillations on the curves are caused by falling drops.

voltages at which the discontinuity occurs: these are discussed below as the "hysteresis" effect. It has to be mentioned that the change of external resistance, *e.g.*, galvanometer and shunt, has no effect upon the sharp shape of the maximum observable in ca. milli-normal electrolytes, even if varied from 1 ohm to 20,000 ohms. With larger resistances the slope of the ascending branch is considerably lowered, showing the electrolytic resistance in the cell in this case of the order of 20,000 ohms. The linear increase of the current (best seen in fig. 9, part A), well marked in very dilute solutions, permits us to calculate directly the internal electrolytic resistance of the cell. To an increase of the applied E.M.F. by 0·500 volt corresponds a linear increase of the current by $3{\cdot}45 \times 10^{-5}$ amp.; this is only possible when the cathode during this interval remains unpolarized and the electrolytic resistance equals $0{\cdot}500 : 3{\cdot}45 \times 10^{-5} = 15{,}000$ ohms. This value is to be expected from the specific resistance of the milli-normal electrolyte (ca. 10,000 ohms) when considering the shape and distance of the two mercury electrodes. Thus at the fall of the maximum the cathodic potential must at once increase by $R.\Delta i = 15{,}000 \times$ (fall of current), which amounts to almost 0·50 volt. Henceforth (in part D) the cathode remains perfectly polarizable, as evident from the constancy of the current during further increase of the E.M.F. (compare [8], *l. c.* p. 264). The same influence of the electrolytic resistance upon the slope of the current is well observable in solutions of electrolytes below milli-normal (*e.g.*, fig. 2, curves 1, 2, 3). This slope, again, increases with the conductance of the solution, according to Ohm's law.

As to the position of the apex of maxima, it is observed that when increasing the concentration of reducible matter the maxima increase, and consequently the apex is shifted to more negative voltages. The increase of the rate of dropping shifts also the apex of a maximum towards a greater polarizing E.M.F.

This is well observable in fig 6, where the apex of the maximum due to pure oxygen (curve 4) occurs at the polarizing E.M.F. 1·550 volts, that due to the atmospheric oxygen (curve 3) at 0·760 volt, and that due to the oxygen content in nitrogen at 0·40 volt (curve 2). The other influence, viz. that of dropping, is visible from the polarogram 9, where curve *a* has been obtained with drops of 3·2 sec., and the curve *b* with drops of 6·7 sec. duration. This at once suggests that the phenomenon of maximum at the current-voltage curve, and with it Kučera's anomaly,

will entirely disappear when using an infinitely slowly-dropping cathode, *i.e.*, a steady mercury surface as it is indeed observed at the smooth electro-capillary parabolas obtained by Lippmann's method, with the stable meniscus in the capillary electrometer.

The Rôle of Concentration-Polarization.

When recording the currents due to polarization of a small steady mercury cathode with the same anode and the same dilute electrolyte solution in which the prominent maxima with the dropping cathode are obtained, no reproducible maxima are observed unless the solution is well stirred. Thus stirring—whether effected by agitation of the solution around a steady electrode surface or by the continual drop formation at the dropping cathode—prevents the decrease of current. When stirring is applied, the decrease of current sets in only at great polarizing E.M.F., whereas with steady electrodes the current is known to diminish quickly at the beginning of the applied voltage. The latter phenomenon is well known to be due to concentration-polarization, *i.e.*, due to the formation of an exhausted layer of solution exhausted from reducible matter, through which layer the reducible matter only diffuses to the electrode, causing thus a small steady diffusion current. It is well known that this concentration-polarization may acquire considerable values, like those of concentration cells. Under the applied E.M.F. any steady electrode surface soon becomes a polarized "old" surface to be distinguished from the "fresh" one, maintained in the original concentration condition by the continual dropping of mercury or good stirring, in which case no concentration-polarization can start. This distinction between the "fresh" (*i.e.*, just being formed) and the "old" interface (*i.e.*, polarized by concentration-polarization) suffices to explain the phenomena of maxima.

Adsorption and Diffusion Currents.

The first consequence of the formation of an exhausted layer at any electrode is a total absence of any adsorption of the reducible matter, because now the interface is isolated from the bulk of the solution by the exhausted layer so that the adsorptive forces at the water-mercury interface cannot penetrate into the bulk concentration, being separated by a water film certainly thicker than 10^{-7} cm., which is regarded as the limit of the action of adsorptive (capillary) forces

We thus may have the advantage of a positive adsorption

of reducible matter at an electrode and of the consequent increase of current only when the concentration-polarization, *i. e.*, the formation of an exhausted layer, is totally prevented by perfect stirring. This is the advantage of the dropping mercury cathode with its fresh interface, which thus allows great currents aided by adsorption. However, this advantage of the adsorption of reducible matter is sustained only within a certain limit of the polarizing E.M.F., owing to the limitation of the rate of adsorption. Hence with increasing voltage the current increases maximally to the value when the rate of reduction of reducible matter is just equal to the rate of adsorption of the reducible matter to the interface; as soon as the rate of reduction exceeds the rate of adsorption, at once concentration-polarization must start at the mercury-solution interface; this removes adsorption entirely, and the current falls suddenly to the value maintained by the ordinary rate of diffusion of reducible matter through the exhausted layer to the electrode surface. The current due to voltages within that at which the maximum occurs (*e. g.*, fig. 9, parts A M) might be denoted as *the adsorption current* to be distinguished from *the diffusion current* occurring at voltages above that of maximum (fig. 9, part D`.

It is also understandable why the concentration-polarization maintained at the dropping mercury cathode when polarizing with decreasing E.M.F. disappears at a smaller voltage (0·495 volt, curve *b*, fig. 9) than when increasing the E.M.F., in which case the discontinuity starts at 0·535 volt. This difference is, no doubt, due to the circumstance that it is easier to maintain the concentration-polarization, if once set up, than to start it if adsorption is displayed. In this explanation we have to imagine the concentration-polarization to be handed over from one drop to the other, which will be the more justifiable the slower the rate of dropping. As will be mentioned later on, small steady mercury cathodes exhibit also maxima, *i. e.*, adsorption and diffusion, currents, provided the solution is kept well stirred in air. When reversing the direction of the polarizing E.M.F. a similar hysteresis appears, but in much greater degree, which is understandable from the above principle of maintaining concentration-polarization when once started*.

The Cause of the Anomalies.

The explanation of the marked changes in the interfacial tension at voltages at which the maximum of the current

* For similar hysteresis phenomena accompanying maxima see the above cited paper of P. Herasymenko, J. Heyrovský, and K. Tančakiský.

occurs is now evident. Any sudden change in the polarization of a mercury cathode causes a corresponding change in the interfacial tension; if, now, the adsorption current changes into the diffusion current, and consequently great changes in the concentration at the interface as well as in the cathodic potential take place, the interfacial tension must accordingly be suddenly altered. Thus in the case of solutions electrolysed open to air, *i. e.*, containing atmospheric oxygen dissolved, the interfacial tension, when the applied E.M.F.'s still allow an adsorption current, is notably different from the interfacial tension due to polarizations at which the concentration-polarization is already established. The transition from the former to the later state of polarization is the cause of Kučera's anomalies. From this point of view it will be clear that in Lippmann's method of capillary electrometer no such anomalies can occur, since at this small stable mercury surface concentration-polarization starts from the very beginning of the polarizing E.M.F. In other words, Lippmann's mercury cathode is always an "old" perfectly polarized interface, widely different in conditions of polarization from those at the "fresh" interface of the dropping cathode at which adsorption phenomena are displayed. Our measurements show an increase of the interfacial tension mercury-solution $\gamma_{1,2}$ when the concentration of oxygen in solutions is increased, and a sudden fall in $\gamma_{1,2}$ when oxygen is—according to the above view—exhausted by concentration-polarization. The simple application of Gibbs's adsorption formula would lead one to expect the reverse—viz. a lowering of surface-tension by positive adsorption at the interface mercury-solution; however, it must be borne in mind that the changes of the interfacial tension $\gamma_{1,2}$ need not obey the simple thermodynamic deductions of Gibbs, which suppose conditions of surfaces chemically unchanged by adsorption. When oxygen comes into the interface, the physical conditions are there complicated (*e. g.*, by an alteration of the distance between the surfaces or the chemical action of O_2 or H_2O_2 at the interface) so that no exact formula is available for the calculation of $\gamma_{1,2}$ from the surface-tension of the solution γ_1, and from the surface-tension of mercury γ_2. Prof. Kučera used in his communication Neumann's formula,

$$\gamma_{1,2}=\gamma_1+\gamma_2-2\,A,$$

where A is the "adhesion" between the two phases, whilst, according to Antonoff, an empirical relationship might be applied:

$$\gamma_{1,2}=\gamma_2-\gamma_1.$$

The latter formula would show why $\gamma_{1,2}$ has to increase if adsorption of O_2 or H_2O_2 lowers γ_1 or increases γ_2; if Neumann's formula were valid, our results would mean that positive adsorption of oxygen at the interface mercury-solution largely diminishes the "adhesion" A between the two phases.

The curious phenomenon that the interfacial tension of mercury decreases when during electrolysis oxygen is removed, has no analogy in changes of interfacial tension observable in maxima due to other electro-reductions, *e.g.*, in solutions of mercury, thallium, nickel, uranyl-salts; it has thus to be ascribed to a chemical action of oxygen or its reduction product, the hydrogen peroxide, upon mercury.

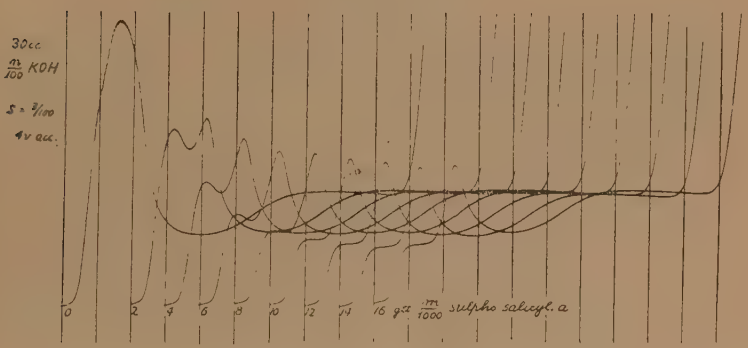
The Suppressive Effects.

The suppressive effect of very dilute adsorbable matter upon the maxima is also easily understandable from the above point of view of adsorption at interfaces. Such substances as organic dyes (fuchsin, eosin, fluorescein, methylene blue, etc.) or aromatic compounds (like benzoic, salicylic, aceto-salicylic, sulpho-salicylic acids) and their salts, and further, higher fatty acids and soaps, adsorb even when present in extreme dilutions (1/500,000 molar) at the mercury solution interface, pushing oxygen out of the adsorption layer (according to Michaelis and Rona's or Freundlich and Losey's displacing action, or Reichenstein's substitution principle), and thus lower the adsorption current due to reduction of oxygen; in other words, they poison the fresh electrode surface, changing the adsorption current into the diffusion one, in which oxygen has to diffuse through the adsorbed layer of surface active matter added to the solution. Electrolytes act similarly to these highly adsorbable substances, but to a much less extent. It is interesting to note that, if the adsorbable matter forms anions, the suppressive effect upon the current-voltage curve becomes most marked at the ascending part of the reduction current in the region where—according to the theory of electro-capillarity—mercury is positively charged against the solution (see fig. 10). Here the series of curves represents the reduction current of a $n/100$ solution of potassium hydroxide standing open to air, in which we notice the maximum due to the reduction of oxygen, first to hydrogen peroxide and then the second stage of the reduction (hydrogen peroxide to water), and, finally, the increase of current due to deposition of potassium. Increasing number of drops of a millimolar solution of

sulpho-salicylic acid were added, and the curve each time repeatedly polarized from zero voltage. We observe the great suppressive effect upon the ascending part of the reduction current, which is very marked already with one or two drops of the millimolar acid added to 30 c.c. (*i.e.*, at a molar dilution of half a million). Of course, when added in such a dilution to an excess of alkali, the acid is present as anions of its salt, to which the suppressive action has to be ascribed. Most marked is this action with soaps, which are known to have very adsorbable anions. On the whole, divalent anions, like sulphate and carbonate, suppress more than anions of monovalent salts of equivalent concentration.

This influence of anions corresponds to what has been found previously in the suppressive action of cations which act

Fig. 10.



upon maxima occurring at very negative cathodic potentials, *e. g.*, in the case of nickel (compare [8]), where the suppressive action of cations considerably increases with their valency.

The removal of the discontinuous fall on the electrocapillary curves effected by addition of small quantities of surface active matter well conforms with the explanation given above, viz. that these substances are adsorbed preferentially to oxygen (compare fig. 8, where the curve *c* is the part of the electro-capillary curve when fuchsin was present in concentration 1/40,000).

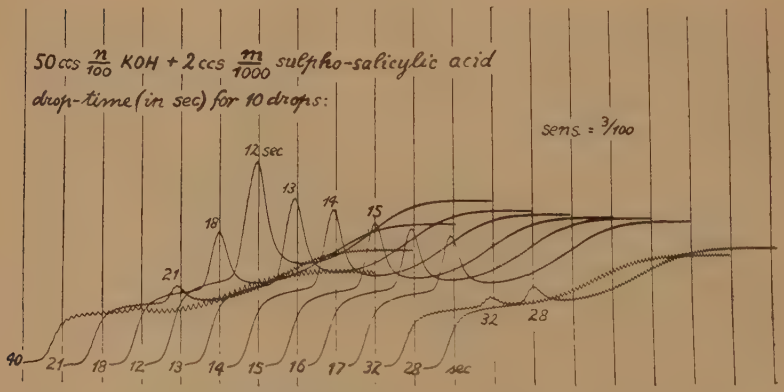
This adsorption must cause a considerable change of interfacial tension, in the same sense as the absence of oxygen, and, of course, allows the concentration-polarization to start from the very beginning of a polarizing E.M.F., just as it is in the Lippmann statical method. Thus in the presence of surface active matters in solution no Kučera' anomalies appear.

Even colloidal solutions show this effect of the removal of the discontinuous fall of electro-capillarity, as has been recently pointed out by Dr. K. Šandera [10], who finds that Kučera's anomalies are suppressed by the presence of colloidal matter. The same is the action of solutions containing freshly-precipitated barium sulphate, which were found to suppress the maximum at the current-voltage curve.

The Effects on Slow Drops and Stable Electrodes.

It has been pointed out that the lowering of the rate of dropping causes the discontinuous fall to appear at decreasing voltages until at infinitely slowly dropping electrodes, *i. e.*, at stable cathodes, it disappears entirely. The mentioned dis-

Fig. 11.



tinction between "old" surfaces, *i. e.*, polarizable by concentration-polarization, and "fresh" ones at which adsorption is displayed, explains also this behaviour, which is best shown in fig. 11. This shows a series of current voltage curves, all obtained from the same solution of 50 c.c. centi-normal potassium hydroxide with 2 c.c. of a millimolar sulpho-salicylic acid. Owing to the surface action of the sulpho-salicylic acid, the oxygen is almost pushed out of the interface, and in this condition adsorption in the interface is particularly sensitive to the rate of the formation of interface—*i. e.*, on dropping. Thus very fresh interfaces (quick dropping) show a still considerable amount of oxygen adsorbed (*e. g.*, curves 4, 5, 6, fig. 11), whilst somewhat older interfaces (twice slower dropping) show almost no adsorption of oxygen (*e. g.*, curves 1, 10, 11, fig. 11). Here evidently the time-effect

consists of the more adsorbable matter gradually pushing out the less adsorbable one—*i. e.*, oxygen. In such a case stable electrodes could not show any adsorbed oxygen, and therefore exhibit no adsorption current but merely a diffusion one being at the same time perfectly polarizable.

Polarographic curves obtained when polarizing a small steady mercury surface exposed to air and using a milli normal electrolyte without any surface active matter, do not show any reproducible maxima, which would be indepen dent of the duration of polarization unless the solution be agitated. When vigorously stirring the solution the same maxima occur on current-voltage curves the position of which is independent of the duration of polarization, and to a small extent it depends on the direction in which we change the polarizing E.M.F. (*i. e.*, the hysteresis effect already mentioned). Here, no doubt, the mercury-electrode surface is kept a "fresh" one by stirring—like the dropping cathode—*i. e.*, it is an electrode at which the concentration-polarization is prevented, and thus the adsorption current manifests itself; when, however, the stirring ceases the concentration-polarization soon starts, the surface being transformed into an "old" one, which is indicated by the sudden fall of the current, exactly similar to the fall which accompanies Kučera's anomaly.

The authors gratefully acknowledge grants of the Czech Academy of Science, which enabled them to carry out these polarographic investigations.

Summary.

1. Current-voltage curves obtained in electrolysis with the dropping mercury cathode when solutions standing open to the air are polarized, show prominent well-reproducible maxima due to the direct electro-reduction of dissolved atmospheric oxygen. The maxima are most prominent and discontinuous in ca. millinormal solution of electrolytes.

2. The fall of the current at the maximum is accompanied by a sudden fall of the interfacial tension at the polarized mercury-dropping cathode and a sudden increase of the cathodic potential.

3. The maxima of the current as well as those of the interfacial tension are suppressed by surface-active matter, active anions, or great concentrations of electrolytes. These phenomena are explained by preferential adsorption.

4. The discontinuous changes of electro-capillarity, which were first described by Prof. Kučera, *i. e.*, "Kučera's

anomalies," as well as the maxima of the current are explained by the setting in of the concentration-polarization, which prevents further adsorption of oxygen at the mercury-solution interface. Similar current maxima are well observable on small stable mercury cathodes when the solutions are stirred.

References.

(1) Jar. Heyrovský, Phil. Mag. xlv. p. 303 (1923).
(2) B. Kučera, *Annalen der Ph.* iv. 11, pp. 529, 693 (1903).
(3) B. Kučera, *Bulletin international de l'Académie des Sciences de Bohême*, 1903.
(4) J. Rasch, Dissertation, Charles University, 1928.
(5) Jar. Heyrovský and collabor., *Rec. des trav. chim. des Pays-Bas*, xlvi. pp. 488-607 (1925).
(6) Jar. Heyrovský, Transactions of the Faraday Society, xix. p. 692 (1924).
(7) P. Herasymenko, Transactions of the Faraday Society, xxiv. p. 267 (1928).
(8) N. V. Emelianova and J. Heyrovský, Transactions of the Faraday Society, xxiv. p. 257 (1928).
(9) J. Heyrovský, *Časopis československ. lékárnictva*, vii. p. 224 (1927).
(10) K. Šandera, *Rozpravy II. tr. České Akademie*, xxxvi. no. 58 (1928).

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CX. *On the Ionization of Hydrogen by its own Radiations.* *By* John Thomson, *M.A., B.Sc., Carnegie Research Fellow in the University of Glasgow**.

Introductory.

In a recent paper † the writer described a preliminary investigation of the ultra-violet ionizing radiations emitted by point discharges in various gases. Experiments performed in hydrogen appeared to indicate that this gas was ionized by its own radiations, and attention was called to this rather remarkable phenomenon in the discussion of the results. The experiments then described, however, were not primarily intended to investigate this effect, and did not appear (to the writer and others) to be absolutely conclusive. There was a possibility that the ionization observed was due to traces of water-vapour in the gas or on the electrodes.

* Communicated by Prof. E. Taylor Jones, D.Sc.
† Phil. Mag. vi. p. 526 (1928).

The present communication describes an investigation the sole object of which was to determine if pure dry hydrogen gas is ionized by radiations emitted by a point discharge in the same gas. The results obtained appear to justify the assumptions previously made, showing that the presence of impurities in the gas or on the electrode surfaces is not a necessary condition for ionization to occur. In a note at the end of the paper the experiments of Chattock and Tyndall on the electrical wind in hydrogen are discussed with reference to the present investigation.

Experimental Methods.

It may be well to indicate briefly the theory of the experiments described in the previous communications. The radiations investigated are of such a nature that the only solid substance through which they are transmitted with sufficient intensity to be detected is a celluloid film. Consequently the radiations were produced and detected in the same tube. The point discharge took place in the region P of the discharge-tube. The radiations emitted were detected by their ionization and photo-electric effects in the region Q. Between P and Q an arrangement of shields was placed to ensure that no ions could travel from the discharge to the ionization chamber. Examples of such tubes for producing and detecting the radiations are given in figs. 1 and 2 of the present paper and in fig. 1 of the previous communication.

The first series of experiments was made, using discharge tubes which had not been "baked out." The aim of these experiments was to trace any changes which might occur in the ionization current at Q due to the radiations emitted at P, as the gas, walls, and electrodes became gradually free from water-vapour and gases other than hydrogen. In order to obtain the necessary insulation in such a tube, filled with moist gas, it was necessary to use a wax sealing round the electrode which measured the ionization current. Consequently such a tube could not be "baked out" at any stage of the investigation.

The second series of experiments was therefore performed with a different set of tubes. These tubes were "all glass and metal-seal-in," so that they might be "baked out" at a high temperature. By this means the attempt was made to measure the ionization current at Q when the tube and electrodes had been thoroughly dried and "outgassed," the hydrogen which was admitted being pure and dry.

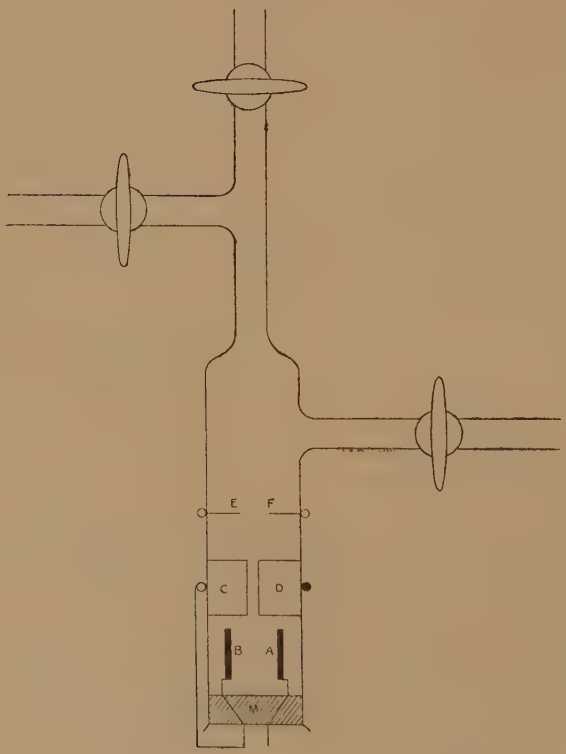
Lastly, it must be mentioned that all these experiments were performed at approximately atmospheric pressure, thus

removing many of the dangers of impurities which arise when the pressure is low.

Unbaked Tubes and Electrodes.—The first set of experiments was made with the discharge-tube represented diagrammatically in fig. 1.

A glass cylinder 2 cm. in diameter was connected to three side-tubes. These led to the pump, the mercury pressure-

Fig. 1.



gauge, and the gas system. E and F were the points of two platinum electrodes, half a centimetre apart, and between them the discharge passed. Throughout all the experiments the discharge current was maintained at 1 milliamp. C and D were two brass half-cylinders arranged to prevent the passage of ions from the discharge to the ionization chamber. The slot between them was 2 mm. wide and the cylinders were 2 cm. long. The ionization chamber contained the two rectangular electrodes A and B, the former

being connected to the electrometer. These electrodes were so arranged that no radiation from EF fell *directly* upon them. That they would collect scattered radiation cannot be doubted.

The tube was sealed at M with a mixture of beeswax and resin. While experiments were being performed, C and B were at a potential of −380 volts with respect to A, which was initially at earth potential. The potential of D was +300 volts relative to the earth. The lead from A to the electrometer was carefully shielded.

The gas was obtained by the electrolysis of barium hydroxide in a specially constructed Hoffmann's apparatus. The anode was placed half-way up one of the arms at a distance of 30 cm. from the bottom. There was therefore no possibility of any diffusion of oxygen into the hydrogen arm. The gas then passed through a liquid-air trap and a capillary tube to the discharge apparatus. The pump used was a Cenco Hyvac, since very low pressures were not required.

As already stated, the method of investigation adopted was to attempt to dry the gas and discharge-tube progressively by means of liquid air. Starting with moist gas, readings were taken of the ionization current at A when the discharge was passing at EF. Then liquid air was placed round the trap, and the dry gas was passed into the tube. Here it no doubt received water-vapour from the walls and electrodes and became relatively moist again. A reading of the ionization current was again taken. This process of admitting dry gas and of measuring the ionization current was continued for some considerable time until the ionization current became constant.

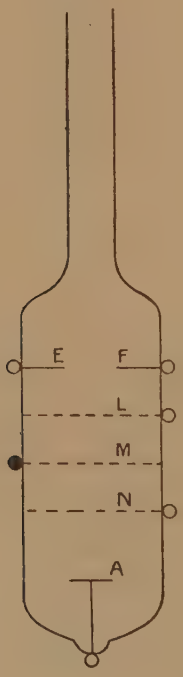
The results of this experiment are shown in the table below. The column "No. of experiment" indicates the order in which the experiments were taken: 1 and 2 refer to moist gas; during 3 to 10 the gas was being progressively dried by the method indicated above.

No. of experiment...	1	2	3	4	5	6	7	8	9	10
Ionization current...	3	3	4	8	21	30	42	56	56	56

After the ionization current had become constant, a series of readings was taken of the current at different pressures. These readings gave a curve in remarkable agreement with that obtained using moist gas, and obtained under the same conditions (curve (*a*) in fig. 2 of the previous paper).

Similar experiments were attempted with different discharge-tubes designed to prevent *any* radiation from EF impinging upon A or B. The elaborate precautions which were necessary, however, caused A and B to be removed too far from the discharge, and narrowed the beam of radiation greatly. The results with such tubes were never satisfactory on account of this weakening in the intensity of the radiation between A and B. Disturbing effects which were ultimately

Fig. 2



traced to charge on the walls and the relatively large distance between A and B became prominent. This type of experiment had to be abandoned.

Baked-out Tubes and Electrodes.—The second experiment required a tube of the "all glass and metal-seal-in" type. This is represented in fig. 2. Every precaution was taken to ensure that no impurities of any description would interfere with the investigation. The gas system was similar to that used previously, except that another liquid-air trap was inserted between the capillary tube and the

discharge-tube. No mercury gauge was used, and a single two-way vacuum stop-cock connected the pump, gas system, and discharge-tube. All the connexions were glass-sealed.

In the tube itself, L, M, N were disks of wire gauze, and A was a small copper plate. These were heated strongly before they were sealed into the tube, to remove as much occluded gas and vapour as possible. Then the tube was placed in a small electric furnace and baked out at about 350° C. for about 4 hours at a high vacuum. As the tube cooled it was immersed in a paraffin-wax bath in order to coat the outer surface of the glass with a good insulator. Pure dry hydrogen was then admitted to approximately atmospheric pressure.

As in the previous work, the discharge current of 1 milliamp. passed between the points of the platinum electrodes E and F. The gauze L, which was at a distance of 1 cm. from EF, was maintained at a potential of +300 volts relative to the gauze M. The latter was 1 cm. from L and at earth potential. The gauze N, 1 cm. below M, was maintained at −370 volts, while the plate A, connected to the quadrant electrometer and initially at earth potential, was 1·4 cm. from N. This arrangement of potentials and distances effectively screened the plate A from any currents due to ions produced above the gauze N. It also prevented the passage of photo-electrons from N to A, since the field between N and M was greater than that between N and A.

Experiments with this apparatus showed that when the discharge was passed across the gap EF, the plate A became charged negatively. This current ceased immediately after the discharge was cut off. It appeared to be a true ionization current due to the gas between N and A. The current remained very constant when the discharge current remained constant. It appeared to be quite independent of the number of times that the discharge had already been passed. Moreover, as in a former experiment described in the previous paper, the ionization current increased linearly with the discharge current, as the latter was varied between 0·4 and 1·6 milliamp.

Analysis of the Results.

It appears to the writer that the first series of experiments admits of only one interpretation. The only effect of placing the liquid air round the trap was to dry and purify the gas. As the gas, tube, and electrodes became drier, the ionization increased. The ionization, therefore, must be due to the

gas itself. The explanation of the increase in the current may be interesting, but as far as the present experiments are concerned, it is a matter for conjecture. That the result is not quite anomalous is shown by the peculiar results obtained by Chattock and Tyndall * on the electrical wind in very pure hydrogen. These writers have shown that when the gas is very pure, there is a large apparent increase in the velocity of the negative ions emitted by the point in a point-to-plane discharge. That their results are closely connected with those of the present investigation is shown at the end of this communication.

The second experiment is even more conclusive. The currents measured were very large indeed, and remained constant over a large number of experiments. This suggests that no changes were taking place in the gas-content of the tube, an effect which had caused considerable difficulty during earlier observations.

Theoretical Considerations.—The result of the investigation appears to the writer to be of some theoretical importance. In the paper already mentioned † attention was directed to the fact that F. L. Mohler ‡ was unable to detect any photo-ionization of hydrogen by its own radiations. His experiments were performed at a pressure of about 0·02 mm., however, and his result is not necessarily contradictory to that of the present investigation. The conclusion which he draws from his experiment is that, not only are H_2 and H unable to emit radiation capable of directly ionizing H_2, but that H_2^+ has also an ionizing potential which is less than 15·9 volts.

From the present experiments no conclusion of this nature regarding ionization potentials can be drawn. If it could be assumed that the gas in the ionization chamber was normal hydrogen and that the ionization took place in one stage, then the result would contradict Mohler's conclusion; but neither assumption is justifiable. The high pressure in the ionization chamber favours interchanges of energy between excited molecules; and it appears to the writer that this is the most probable explanation of the observed ionization. Having regard to Mohler's conclusion, it may be asserted that the ionization is brought about by two-stage excitation, due to molecules absorbing two or more quanta of energy, either from the radiations or by collisions with excited molecules.

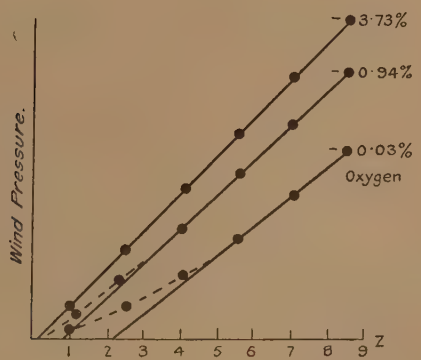
* Phil. Mag. xix. p. 449 (1910).
† Thomson, *loc. cit*,
‡ Proc. Nat. Acad. Sci. xii. p. 494 (1926).

Note on the Investigation by Chattock and Tyndall of the Pressure of the Electrical Wind.

The writer's attention was called to this investigation by Professor Tyndall at the Glasgow meeting of the British Association. The primary object of the experiments was to determine the velocity (V) of gas ions in a field of 1 volt/cm. "Earlier measurements by the wind-pressure method* led to values of V which are in satisfactory agreement with those obtained by other methods," but in the particular case of hydrogen the velocity of the negative ions varied very considerably with the purity of the gas.

It may be well to sketch briefly the theory of the experiment. A controlled current of a few microamperes flowed

Fig. 3.



from a sharp platinum point A to a circular perforated plate B, the point and plate being enclosed in an air-tight tube. By means of the sensitive manometer invented by one of the authors for this purpose, it was possible to measure the pressure of the electrical wind at the plate B. A could be moved so that the distance AB (z) could be varied. The experiment consisted in measuring the pressure of the wind p for different values of z, and by this means obtaining $\frac{dp}{dz}$. This allowed the specific velocity of the ions to be calculated.

The curves shown in fig. 3 (curves II. in the communication of Chattock and Tyndall) were obtained by plotting

* Phil. Mag. i. p. 79 (1901).

p against z, each curve corresponding to a different percentage of oxygen impurity in the gas. In each case, when z is large $\frac{dp}{dz}$ is constant, and this is the result predicted by the authors' theory. It will be noted, however, that as the hydrogen becomes purer, $\frac{dp}{dz}$ decreases, while z_0, the intercept on the z-axis made by the straight part of the curve produced, increases. Chattock and Tyndall explain the decrease in $\frac{dp}{dz}$ as the gas becomes purer by the hypothesis that there is back-discharge from the plate to the point, and this discharge increases as the percentage of oxygen impurity decreases. How the back-discharge is produced they do not suggest.

Two possible explanations are given by the authors of the increase in z_0 which accompanies the decrease in oxygen impurity, viz. :—

(i.) "The ions from the point may travel an appreciable distance before growing large enough to produce much wind."

(ii.) "The gas may be ionized for an appreciable distance from the point—this being equivalent to a lengthening of the point as far as wind-production is concerned."

Both of these phenomena are supposed to be enhanced as the gas becomes purer.

The purpose of the present note is to suggest an explanation of the manner in which the back-discharge in these experiments arises, and of the reason why it increases as the gas becomes purer. The same explanation accounts for the existence of z_0, and for its increase as the oxygen impurity diminishes.

It has been shown by Wynn-Williams * and the present writer † that a metallic point such as that used by Chattock and Tyndall gives rise to electromagnetic ionizing radiations. These have been shown to emanate, not from the point itself, but from the gas in its immediate vicinity, and in the case of an air discharge from gas within 2 to 3 mm. from

* Phil. Mag. i. p. 353 (1926).
† *Loc. cit.* v. p. 513 (1928).

the point. In air such radiations can produce ionization up to a distance of about 3 cm. from their source; beyond his they cannot be detected. It has also been shown that the intensity of the radiations is a linear function of the current flowing in the discharge.

This, then, appears to afford the explanation of the back-discharge postulated by Chattock and Tyndall. Considering first the case of impure hydrogen, z_0 is of the order of 4 mm. and the back-discharge is small. Even in this case, however, the writers found that $\frac{dp}{dz}$ increased as the current in the discharge decreased. This certainly indicates the existence of back-discharge. Moreover, it may be correlated with the fact mentioned above that the intensity of the ionizing radiations increases linearly with the discharge current.

The authors explain the normal z_0 (4 mm.) by means of Franck's hypothesis that the ions do not reach their full size while travelling a distance comparable with 4 mm. They find it difficult, however, to explain by this supposition the increase in z_0 as the gas becomes purer. A satisfactory explanation may be given in terms of the ionizing radiations. In order that radiation may occur, recombination or at least inelastic impact of ions with molecules must take place. Hence, within a distance of 3 mm. from the point, many of the ions will lose their charge or their velocity. But the radiations emitted in this region would cause ionization, and in a short distance the excess of negative ions would be re-established. This would account for the existence of z_0, and an examination of the results given in the previous paper by the present writer will show that the theory can be applied to both positive and negative discharges in air or in hydrogen.

The most interesting phenomenon, however, from the point of view of the present paper is the decrease in $\frac{dp}{dz}$ and the increase in z_0 as the hydrogen becomes purer. It has been shown earlier in the present communication that the ionization in hydrogen, due to radiations emitted by a point discharge in the same gas, increases enormously as the gas is purified. In the experiments described the impurity was water-vapour, but it must be remembered that the passage of the discharge would decompose part of the water and cause oxygen impurity. It is indeed remarkable that this result should agree so well with the experiments of

Chattock and Tyndall. The increase in back-discharge as the gas became purer, the increase in z_0 from 4 mm. to 3 cm., are exactly what would be expected if the radiations became more intense and the gas itself a more perfect absorber. There appears to be no doubt that radiation is more easily excited in the pure gas, since the authors observed that "in the purest hydrogen and for a negative point the whole plate glows brightly over the surface presented to the point." At the end of their communication they remark: "The four phenomena of glow, fall of wind-pressure, shift of negative curve (increase of z_0), and abnormally rapid combination, all take place within about the same narrow limits of oxygen percentage; it is therefore at least tempting to think that they may all ultimately prove traceable to a single source." It appears to the writer that this source is to be found in the variations in the intensity of the radiations emitted by the gas in the vicinity of the point during the discharge.

Summary.

1. Experiments are described showing that hydrogen is ionized by radiations emitted by a point discharge in the same gas. It is suggested that the ionization takes place in stages, the molecules absorbing two or more quanta of energy, either from the radiations or by collisions with other excited molecules.

2. The results of this and preceding investigations by the same writer are applied to the investigation by Chattock and Tyndall of the pressure of the electrical wind. It is shown that several peculiar phenomena encountered by these experimenters can be satisfactorily explained by a consideration of the ionizing radiations emitted by the gas in the immediate neighbourhood of metallic points charged to a high potential.

In conclusion, the writer again wishes to express his indebtedness to Professor Taylor Jones for his advice and encouragement. He also wishes to thank the Carnegie Trust for a much-appreciated grant for apparatus.

February 1929.

CXI. *The Effect of Stress upon the X-Ray Reflexions from Tungsten Wire at Air Temperature.* *By* H. L. Cox, *B.A.*, *and* I. Backhurst, *M.Sc.* (*both of the National Physical Laboratory*)*.

[Plate XXII.]

Introduction.

In connexion with fundamental research on the deformation of metallic single crystals, it appeared to be of interest to determine whether the application of stress to a single crystal was capable of producing elastic deformation of the space lattice either in part or in whole. Should the lattice as a whole be distorted, evidence of the distortion could be obtained by recording the relative movements of the crystallographic planes as determined by X-ray examination. Should only portions of the lattice be affected, *e. g.*, by deformation in the neighbourhood of cracks, the distortion would be evidenced by a blurring of the spots obtained by reflexion of X-rays from the crystallographic planes. In either case the crucial point would be whether, upon removal of the stress, the X-ray diagram obtained returned to its original appearance before the stress was applied.

With this object in view, it was decided to take X-ray photographs of a single crystal, firstly unstrained, and then under a series of stresses of gradually increasing magnitude. It was intended to watch each successive photograph for any change in appearance, and, as soon as any alteration was remarked, to take a final photograph in the unstrained state in order to determine whether the change was permanent.

Description of Experiment.—In order to obtain photographs that would permit of easy comparison with each other, it was decided to take Laue diagrams, the crystal throughout the test being held fixed relative to the X-ray beam.

Since the crystal tested was required to have an appreciable elastic range, tungsten appeared to be the most suitable material (the specimen used in the present experiment behaved elastically up to a normal tensile stress of about 90 tons per square in.). This material was obtainable as single crystals in wires up to 0·9 mm. diameter †. Finally, it was

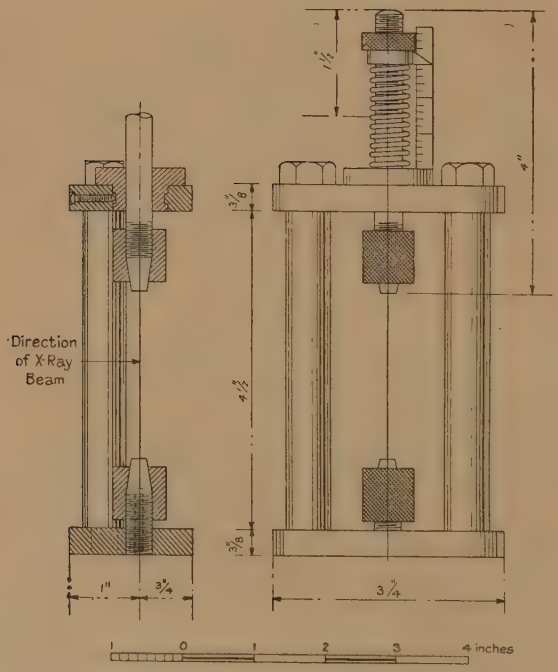
* Communicated by Sir J. E. Petavel, K.B.E., F.R.S.

† These single crystal wires were kindly supplied by the General Electric Company, to whom the authors wish to express their thanks.

decided to use a tungsten single crystal wire of 0·2 mm. diameter, the small diameter being chosen both in order that the high stresses required should be easily obtained, and in order that the X-ray reflexions from the crystallographic planes should give sharp well-defined spots.

A special straining apparatus was designed (fig. 1) in which the tensile load on the specimen was measured by a

Fig. 1.



Apparatus for straining wires during X-ray analysis.

spring, previously calibrated against dead-weight loading. The length of the specimen used was approximately 3 inches between the chucks, and the specimen was examined approximately in the middle of this length, the direction of the X-ray beam being normal to the straining axis.

It was subsequently found that the portion of the specimen used was composed of more than one crystal; but at the section examined there was one main crystal with some

indications of a second orientation. The changes of orientation to which reference is made below refer throughou to the main crystal. It is, of course, obvious that the presence of a small secondary crystal cannot have affected the shape of the spots due to reflexions from the main crystal.

Photographs were taken at stresses from 2 tons per sq. in. normal tension upwards, the increases in stress being made in steps ranging from 2 to 9 tons per sq. in. Each successive photograph was carefully inspected for any alteration in appearance ; but no definite change was observed until a stress of 97 tons per sq. in. had been reached, when it was obvious, from the large bodily movements of the spots, that the material had deformed plastically. A further photograph was taken at 104 tons per sq. in. and a final photograph at 1 ton per sq. in., and a comparison of these two showed that they were identical (Photos Nos. 23 and 24).

All the photographs at stresses up to and including 88 tons per sq. in. were then compared quantitatively, and the change of orientation between each pair of successive photographs was determined. In a visual comparison of the photographs allowance must be made for the fact that the distance of the photographic plate from the specimen was increased from 2·61 cm. to 3·00 cm. between the photographs taken at 34 and 36 tons per sq. in.

A complete record of all the photographs taken is given in Table I. below, while photographs Nos. 4, 20, 21, 22, 23, and 24 are reproduced in Pl. XXII.

The three rotations about the straining axis were all anti-clockwise when viewed from above. Probably therefore they were not due to actual rotational movement of the straining head as the load was increased. On the other hand, the actual movements are so small that it is doubtful whether they lie outside the range of possible errors.

Conclusions.—Beyond the small bodily movements recorded above, no definite alteration in appearance of the Laue diagrams was observed until marked plastic deformation had occurred (Photo No. 22). The previous photograph (No. 21) showed a very slight broadening of the spots. If, as appears probable, this broadening was the beginning of the plastic broadening shown in photograph No. 22, then the elastic broadening, if it occurs, must be too slight to photograph successfully. If, on the other hand, the slight broadening in photograph No. 21 would have disappeared upon removal of the load, then it might be possible to obtain

successful photographs ; but, even if this is the case, the range in which the effect would be visible is extremely small (*e. g.*, in the present experiments it was not greater than 88 to 97 tons per. sq. in.), and very careful calculations would have necessarily to be made beforehand to ensure that, for the particular orientation of the specimen used, this narrow range of stress was not exceeded.

TABLE I.

No. of photograph.	Stress (tons per sq. in. normal tension).	Change of orientation from previous photograph.
4	2	—
5	4	None.
6	7	„
7	18	„
8	27	1° rotation about straining axis.
9	32	None.
10	34	„
11	36	Plate distance altered ; otherwise no change.
12	38	None.
13	41	„
15	45	„
17	53	„
18	62	„
19	71	„
20	80	0·5° rotation about straining axis.
21	88	0·5° „ „ „
22	97	Large plastic movement.
23	104	Further plastic movement.
24	1	No change.

This work is an item in the research programme of the Sub-Committee on Elasticity and Fatigue of the Aeronautical Research Committee. The authors wish to express their thanks to the Committee for the opportunity to carry out this research and for permission to publish the results.

CXII. *The Determination of the Dielectric Constants of Imperfect Insulators.* *By* R. T. Lattey *and* O. Gatty *.

IN determining the capacity of a condenser at high frequencies, neglect of the inductance of its leads may cause serious error; moreover, since no dielectric is a perfect insulator, it is also necessary to introduce corrections for the effects of leakage. No condenser can thus be supposed to be pure capacity, but consists of the parts shown in fig. 1. It can, however, be represented by either of the equivalent arrangements shown in figs. 2 and 3, where

$$\frac{\mathrm{K}}{k}=\frac{1+p^{-2}k^{-2}x^{-2}}{1-p^2kl(1+p^{-2}k^{-2}x^{-2})}=1+p^2\mathrm{K}l+\frac{p^2\mathrm{K}(\mathrm{R}-r)^2}{1+p^2\mathrm{K}l}, \quad (1a)$$

$$\mathrm{R}=r+\frac{x}{1+p^2k^2x^2}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1b)$$

and

$$\mathrm{X}=\frac{x^2(1-2p^2kl)+2xr+(r^2+p^2l^2)(1+p^2k^2x^2)}{x+r(1+p^2k^2x^2)}, \quad \ldots \quad (2a)$$

$$\mathrm{K}'=\frac{k-l(p^2k^2+1/x^2)}{(r^2+p^2l^2)(p^2k^2+1/x^2)+1+2r/x-2p^2kl} \quad \ldots\ldots \quad (2b)$$

Fig. 1.

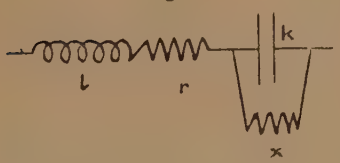


Fig. 2.

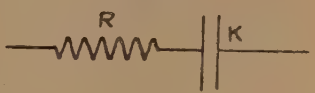
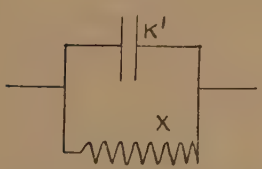


Fig. 3.



Bridge and resonance methods invariably admit of the direct evaluation of either K or K′. But if the effect of changing the dielectric in a condenser is to be used to deduce a dielectric constant, it will not be sufficient to correct K or K′ so as to obtain k, the capacity of the condenser

* Communicated by the Authors.

system. For k must necessarily include a term k_l, which represents the capacity of the leads; every condenser has, too, a capacity relative to its surroundings which we may designate its "earth-capacity," and this part of the capacity is partly fixed and partly dependent on the dielectric in the condenser. Hence the total capacity actually measured will include that of the leads and the earth-capacity. If k_0 is the capacity of the condenser *in vacuo*, while A and B are constants and D is the dielectric constant of the fluid such that the measured capacity is k, then

$$k = k_l + Dk_0 + AD/(B+D).$$

The corrections to be applied to observed values may thus be regarded as:

(1) The capacity of the leads (see 16, 22, 28, 50, 55, 59, 63, 66, 78, 82).

(2) The inductance of the leads (see 75).

(3) The conductance of the dielectric or leakage (see 18, 22, 24, 25, 30, 35, 59, 62, 68, 74).

(4) The earth-capacity (see 22, 66, 75).

(5) Correction for the resistance of the leads.

Attempts to make allowance for these sources of error have been made by a variety of methods, some based on purely theoretical calculation and some on methods of substitution; but very few, if any, investigators have attempted to correct for all.

Considering first the evaluation of k, the capacity of the condenser system, equations (1*a*) and (1*b*) show that it will be practically always justifiable to neglect r. l, however, cannot be neglected even when it is small, as the following example will show. Two parallel straight wires, 1 mm. in diameter and 10 cm. each in length, at a distance of 3 cm. apart, have an inductance of 18×10^{-20} e.s.u. when carrying high-frequency currents in opposite directions. If these are used as leads to a condenser of 1000-cm. capacity, and if the frequency corresponds to a wave-length in air of 200 metres, then the effective capacity of the condenser will be

$$1000/0{\cdot}984 = 1016 \text{ cm.}$$

If the condenser were then filled with a fluid whose dielectric constant was 2·3, its effective capacity would be 2300/0·9634, giving an uncorrected value for the dielectric constant of 2·35. If a frequency corresponding to a wave-length

of 50 metres in air were used, the apparent dielectric constant would be given by

$$(2300/0{\cdot}415) \div (1000/0{\cdot}745) = 4{\cdot}13.$$

Thus it seems likely that neglect of the inductance of the leads may account for many of the supposed variations of dielectric constants with frequency which have been recorded by certain investigators and contradicted by others. Methods for evaluating l will be considered later.

Unless the leakage resistance x is very large and its equivalent R correspondingly small, it introduces certain very serious difficulties into Bridge methods for estimating capacities; for, if a balance is to be secured in such a case, either very large resistances must be used in the ratio arms or else the frequency must be very high. In the first case, the total current being small, the zero is correspondingly difficult to detect, and in the second case difficulties due to induction are increased and elaborate screening must be used. On high-frequency bridges a small total current is especially fatal, since the detector used, unlike the corresponding direct current galvanometer, is usually of such a type that its readings depend on the square of the current, and so correspond to a very low sensitivity in the neighbourhood of zero.

The alternative is to use "tuned circuit" methods, and as these depend on the selection of a position of maximum current, they can be made very sensitive. It is usual to adjust so that the current in the circuit is a maximum, *i. e.*, so that $p^2\mathrm{KL}$ (fig. 4) is equal to unity; the true capacity of the condenser system must then be found by equation (1 *a*). The usual procedure is to adjust the circuit by means of a well-insulated variable condenser K_1, and then to connect the unknown capacity in parallel with the variable capacity and to readjust the latter until resonance is again obtained (fig. 5). The condition for this is that

$$\mathrm{K} + \mathrm{K}_1 = \mathrm{K}_0 \frac{1 - \mathrm{K}_1/\mathrm{K}_0}{1 - \mathrm{K}_1/\mathrm{K}_0 - p^2\mathrm{K}_0\mathrm{K}_1\rho}, \quad \cdot \cdot \quad (4)$$

where ρ is the apparent resistance of the condenser system and is given by

$$\rho = \frac{\mathrm{RK}^2}{(\mathrm{K} + \mathrm{K}_1)^2 + p^2\mathrm{K}^2\mathrm{K}_1{}^2\mathrm{R}^2}. \quad \cdot \cdot \cdot \cdot \quad (5)$$

K_0 is the value of the variable condenser when adjusted for resonance in the absence of K, while K_1 is the corresponding value after introducing K.

As before, K is not the true value of the unknown capacity, but that given by equation (1*a*). Moreover, K_1 and K_0 are not the true capacities of the variable condenser, since the inductance of its leads cannot be neglected at high frequencies. The scale readings must be corrected to give the effective capacities of the variable condenser, and these values be substituted in equations (4) and (5). The correction is effected by equations (1*a*) and (1*b*), putting $R-r=0$, i. e. $x=\infty$.

Observations made by the maximum current method thus require a considerable amount of correction in order to obtain the true value of the capacity of a condenser. The evaluation of the correction for resistance can be made by a method worked out by one of us (35) ; but on the whole it seems preferable to seek a method which does not involve so

Fig. 4.

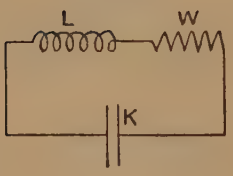
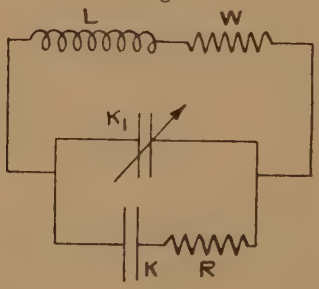


Fig. 5.



much correction. This is found in the method of tuning for maximum difference of a potential described below. It might be described as "Voltage Tuning," in contrast to the more usual "Amperage Tuning *."

* After the theory of voltage-tuning had been worked out by us and while the experimental part of this work was in progress two papers appeared which showed that, in broad outline, our views had been anticipated.

Jezewski (*Zt. f. Phys.* xlviii. 1928, p. 123) showed that voltage resonance at the terminals of a leaky condenser is independent of the leakage-resistance, but he did not examine in any detail the methods for detecting the point of resonance, nor did he consider the effect of the inductance of leads.

Kniekamp (*Zt. f. Phys.* li. 1928, p. 95) evolved the same theory, and applied it to finding the dielectric constants of solutions of sugar and of urea in water, measuring the voltage at the condenser terminals by means of an idiostatic thread electrometer.

The first suggestion of the theorem seems to have come from Tank (*Phys. Zt.* xvii. 1916, p. 114), but his statement is made without detail either mathematical or experimental.

In order to determine the Potential Difference between the terminals of a condenser it is necessary to connect them to something equivalent to a voltmeter. Investigation of the conditions favourable to maximum sensitivity shows that this voltmeter should have a low resistance and should therefore be coupled to the circuit through a condenser rather than through an inductance. For high-frequency work the only practical galvanometers depend on heating effects, and must therefore have some resistance; denoting this by G, it is required to find its optimum value. The circuit may be

Fig. 6*a*.

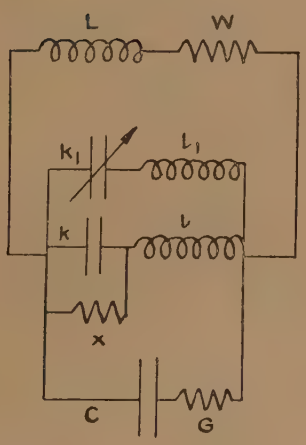
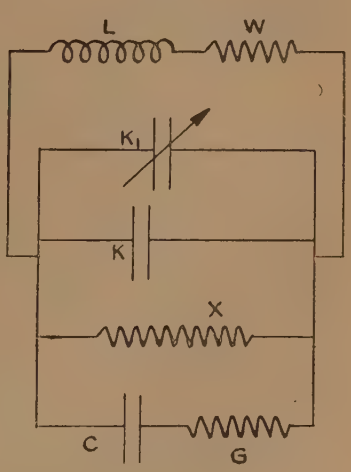


Fig. 6*b*.



represented schematically by fig. 6*a* or 6*b*, and the condition for maximum current in G is

$$K_m + K + \frac{C}{1+p^2C^2G^2} = K_0 + \frac{C}{1+p^2C^2G^2} = \frac{L}{r^2+p^2L^2}, \quad (6)$$

where K_0 is the value of the variable capacity giving maximum current in G when K and X are absent, and K_m is the corresponding value when K and X are present.

Neglecting the resistance of the condenser leads, equations (2*a*) and (2*b*) become

$$X = x(1-p^2kl)^2 + p^2l^2/x, \quad \ldots\ldots \quad (7a)$$

$$K' = \frac{kx^2(1-p^2kl)-l}{x^2(1-p^2kl)^2+p^2l^2} = \frac{k(1-l/kxX)}{1-p^2kl}, \quad . \quad (7b)$$

and these approximate to

$$X = x(1-p^2kl)^2, \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

$$K = k/(1-p^2kl) \quad . \quad . \quad . \quad . \quad . \quad (8b)$$

for all values of p, k, l, x which are likely to occur in practice. Thus K is independent of x for all practical purposes, and by tuning for maximum voltage the necessity for applying a correction for conductance in the dielectric is abolished.

If we denote the current observed in G when $K_1 = K_m$ by I_m, and the current when K_1 is detuned by an amount $(K_m - K_1)$ by I_1, it may be shown that

$$\left(\frac{I_m}{I_1}\right)^2 = 1 + \left[\frac{p(K_m - K_1)}{\frac{1}{X} + \frac{W}{W^2+p^2L^2} + \frac{p^2C^2G}{1+p^2C^2G^2}}\right]^2, \quad . \quad (9)$$

from which it is clear that

$$\frac{1}{pX} + \frac{W}{p(W^2+p^2L^2)} + \frac{pC^2G}{1+p^2C^2G^2}$$

should be small so as to give sharp tuning. For values that are likely to occur in practice this expression approximates to

$$\frac{1}{pX} + \frac{W}{p^3L^2} + pC^2G \quad \text{or} \quad \frac{1}{pX} + pW(K+K_m+C)^2 + pC^2G,$$

and it is thus clear that W, C, and G should all be small. When X is comparatively small it may be advantageous to increase the frequency p ; but this should be avoided, if possible, since it increases the correction terms indicated by equation (8*b*).

If the ratio (Voltage induced in Circuit) to (Current in G) be denoted by Z, then the minimum value of Z is

$$Z_m = \frac{1}{pC}\left(\frac{1}{X} + \frac{W}{W^2+p^2L^2} + \frac{p^2C^2G}{1+p^2C^2G^2}\right)$$

$$\sqrt{W^2+p^2L^2}\,\sqrt{1+p^2C^2G^2}\,; \quad (10)$$

and, as it is clearly desirable that this should be small, G may be taken as variable in order to find a minimum value for Z_m. This gives

$$\frac{1}{X} + \frac{W}{W^2+p^2L^2} = \frac{p^2C^2G}{1+p^2C^2G^2}$$

or approximately

$$\frac{W}{p^2L^2} \equiv p^2W(K+K_m+C)^2 = p^2C^2G,$$

or

$$\frac{K+K_m+C}{C} = \sqrt{\frac{G}{W}}.$$

This was checked experimentally, using air condensers for which X may be taken as infinite. G was a heating wire whose resistance was known to be about 8 ohms. The wavelength in air was 157 metres, corresponding to a frequency 12×10^6. The maximum value of C available was 0·5 MMF. and that of K 1·0 MMF. W was made small and was estimated to be of the order of 1 ohm. Hence approximately

$$pCG = 12 \times 10^6 \times 0{\cdot}5 \times 10^{-9} \times 8 = 0{\cdot}048,$$

also

$$pL = [p(K+C)]^{-1} = [12 \times 10^6 \times 1{\cdot}5 \times 10^{-9}]^{-1} = 55,$$

and W^2 is thus to be neglected in comparison with p^2L^2. For practical purposes the formulæ then assume the approximate forms :

$$Z^2 = \frac{L^2}{C^2}\left[\left(p(K+C)-\frac{1}{pL}\right)^2 + \left(p^2C^2G+\frac{W}{p^2L^2}\right)^2\right]$$

$$= \frac{(K-K_m)^2+p^2(C^2G+(C+K_m)^2W)^2}{C^2(C+K_m)^2}$$

and

$$\frac{K-K_m}{[(I_m/I)^2-1]^{1/2}} = p\{C^2G+(C+K_m)^2W\}.$$

A transmitter was kept going as constantly as possible, and C was varied by steps of 0·05 MMF. from 0·115 to 0·465, and the values of X and the function

$$(K-K_m) / \sqrt{(I_m/I)^2-1} = \phi$$

determined at each step ; from the last equation the values of G and and W can be calculated, giving G=10·19 and W=1·50 ohms.

The condensers used for this experiment were not those used in subsequent work and had not been carefully calibrated; consequently no very high order of accuracy can be expected. Taking the value of $C+K_m$ as 0·9375 the formula for calculating ϕ becomes

$$12 \times 10^6(10{\cdot}19\,C^2+1{\cdot}50(0{\cdot}9375)^2),$$

and it will be seen from column 6 that this gives quite reasonable concordance with observation. Theory indicates that I_m should be a maximum when

$$C = (C+K_m)\sqrt{W/G} = 0{\cdot}9375\,(1{\cdot}50/10{\cdot}19)^{1/2} = 0{\cdot}360.$$

Table I. also bears this out. Moreover, since

$$Z_m = E/I_m = p\{C^2G + (C+K_m)^2W\}/C(C+K_m)$$
$$= \phi/C(C+K_m),$$

the value of $I_m \times \phi/C$ should be constant, as is indicated by column 7.

Similar results were obtained at other frequencies, all bearing out the correctness of the formulæ on which the theory of the method described in this paper depends.

TABLE I.

C.	I_m^2.	K_m.	$C+K_m$.	ϕ. found.	ϕ. calc.	$I_m \times \phi/C$.
0·115	30	0·823	0·940	0·0181	0·0174	0·861
0·165	56	0·774	0·939	0·0195	0·0195	0·885
0·215	78	0·724	0·939	0·0216	0·0215	0·886
0·265	92	0·675	0 940	0·0246	0·0244	0·892
0·315	98	0·624	0·939	0·0269	0·0279	0·843
0·365	99·5	0·570	0·935	0·0310	0·0321	0·847
0·415	97	0·515	0·930	0·0362	0·0369	0·859
0·465	89	0·453	0·918	0·0426	0·0423	0·865

In the preceding paragraphs we have treated the capacities used in terms of their equivalents when inductance of leads and faulty insulation are absent. It now becomes necessary to develop means for evaluating the constants involved in equation (1) ; the details of a practical circuit are indicated in fig. 6*a*, where the subscript 1 indicates the calibrated variable condenser, while k, l, and x refer to the capacity inductance and leakage resistance of the unknown capacity. The circuit is assumed to be so loosely coupled to the transmitter that mutual inductance may be neglected.

Evaluation of Inductances l *and* l_1.

If the unknown capacity can be given two values successively without changing its leads, then, if these are k_1'

and k_2' and the settings of the variable condenser are k_0, k_1, and k_2 in absence, in presence of k_1' and of k_2' respectively, it follows from equation (1) that

$$\frac{1}{k_1'} - \frac{1}{k_2'} = \left(\frac{1}{\Delta_1} - \frac{1}{\Delta_2}\right)(1-p^2k_0l_1)^2, \quad . \quad . \quad (11)$$

where $\Delta_1 = k_0 - k_1$ and $\Delta_2 = k_0 - k_2$. If therefore the frequency is varied, the product $[\Delta_1\Delta_2/(\Delta_2-\Delta_1)]^{1/2}$ should be a linear function of p^2k_0, from which l_1 and the left-hand side of equation (11) can readily be obtained.

Two methods were tried for changing k' without changing l. In the first a condenser with rotating vanes was used (an ordinary wireless condenser), set first at one end of its scale and then at the other. The frequency and the main inductance of the circuit (L) were varied over a wide range. In the second method a condenser was used, filled first with water and then with nitrobenzene (any two fluids of which one has about twice the dielectric constant of the other would do). The first method has the possible disadvantage that the inductance of the leads may perhaps change when the vanes are rotated; the second method has the disadvantage that it is not easy to repeat the sequence of frequencies used with absolute accuracy, and there is also a possibility that the dielectric constant of one or both of the fluids used may be a function of the frequency; this is however unlikely at the frequencies used by us. The results of both methods were in substantial agreement, and were subsequently checked by the use of the two small mica condensers, which could be attached by leads so short that their inductance was clearly negligible.

Since wave-meters are more usually calibrated in wave-lengths than in frequencies, it is more convenient to find values for $4\pi^2c^2l_1$ than for l_1, since $p^2l_1 = (4\pi^2c^2l_1)/\lambda^2$.

The results (Table II.) obtained with the rotating condenser may be quoted as an example.

If the condenser to be tested is now inserted and values of Δ obtained at various frequencies and various values of k_0, then l can be evaluated in the form

$$p^2l = 1/k' - (1-p^2k_0l_1)^2/\Delta - p^2l_1(1-p^2k_0l_1). \quad . \quad (12)$$

The true capacity (k') of the unknown condenser filled with any given dielectric is then to be found by the equation

$$\frac{\Delta}{k'} = (1-p^2k_0l_1)^2 + p^2\Delta(l + l_1(1-p^2k_0l_1)). \quad . \quad (12a)$$

Table II.

λ.	k_0.	Δ_1. obs.	Δ_1. calc.	Δ_2. obs.	Δ_2. calc.	$[\Delta_1\Delta_2/(\Delta_2-\Delta_1)]^{\frac{1}{2}}$ obs.	$[\Delta_1\Delta_2/(\Delta_2-\Delta_1)]^{\frac{1}{2}}$ calc.
70·5	472·7	31·63	31·57	187·31	188·46	6·169	6·154
73	544·5	31·64	31·08	185·02	185·60	6·178	6·109
94	1014·6	30·10	30·09	174·90	173·50	6·030	6·030
107	832·4	32·08	32·72	187·03	186·92	6·223	6·293
129	301·3	36·17	36·30	204·81	205·34	6·628	6·636
191	994·7	35·22	35·58	197·62	198·76	6·547	6·578
221	526·1	37·19	36·69	205·03	204·43	6·740	6·685
Inf.	—	—	37·36	—	206·63	—	6·749

As an example we may take a condenser filled with water at 16° C.

Table III.

λ.	k_0.	Δ.	k'.
72	512·3	220·95	225·4
75	549·3	217·4	224·65
87	491·9	229·4	230·7
89·5	904·2	209·2	233·5
106	793·9	217·35	230.1
116·5	1036·0	211·8	230·1
159	614·5	226·6	229·25
174	770·4	226·0	230·3

It will be seen that, while the values of Δ range between 209 and 229, the value deduced for k' only varies from 224 to 231. (This variation of about 3 per cent. is probably due partly to failure in securing absolute constancy of temperature and partly to the fact that the necessity for always filling a condenser to exactly the same depth was not fully realized at the time when these preliminary observations were made.)

Relation between Capacity observed and Dielectric Constant.

It has already been pointed out that the capacity actually measured will include that of the leads and the earth capacity of the condenser; this may be expressed by $k_l + k_0 D + AD/(B+D)$. If k_0 is large, k_l and A may be neglected or their effects minimized by basing calculations on the difference between two settings of a variable condenser.

But if imperfect insulators are to be used, then k_0 cannot be very large, since this would make the leakage conductance correspondingly great and so make observations very difficult.

Our procedure therefore was to find the dielectric constants of a few good insulators by using a variable condenser of large capacity, and then to calibrate our small condensers by the use of these fluids. The liquids actually used were carbon tetrachloride, chloroform, and a mixture of these; the variable condenser was that referred to in Table II. Our small condensers were then tested with air, the above liquids, methyl alcohol, nitrobenzene, and water in them. This gives four cases in which the dielectric constant is known, and four others about which all that is known is that the condensers must be consistent with one another. In this way the following values were deduced :—

Condenser.	X.	Y.	Z.
k_l	0·26	0·26	0·26
A	8·345	6·23	7·85
B	0·94	0·94	0·94
k_0	11·248	6·368	11·266

Assuming that, as all three were of the same form and differed only in length, the edge-correction would be the same for all, then, from their dimensions, X and Z should be equal, and each greater than Y by 4·51 e.s.u. The experimental value of about 4·89 is satisfactory when we bear in mind that the units in which our condensers were graduated were only approximate centimetres.

The condensers X, Y, and Z, with which the main series of observations were made, were of copper silver-plated; this proved satisfactory for certain liquids including cold water; but when hot water was used, the metal was attacked and became visibly tarnished, the conductivity of the water was markedly increased, and its dielectric constant lowered. This gave an apparently different temperature coefficient from that of other observers; but as subsequent observations, using pure silver plates, have given results in accordance with those usually accepted, it is clear that the apparent anomaly was due to a change in composition of the dielectric.

The condensers were in the form of concentric tubes held in place by rods of glass.

Our calibrated condenser consisted of a series of fixed plates which could be brought into circuit by inserting plugs,

as is usually done in resistance boxes ; in parallel with this was a condenser with rotating vanes giving a range of capacity rather greater than that of one plate.

Temperature Coefficients of Dielectric Constants.

For those dielectrics which are not much affected by temperature a simple linear formula is satisfactory ; but those dielectrics like water and the alcohols which have comparatively large dielectric constants, are more profoundly influenced by temperature, and the changes so brought about cannot be represented by a linear law. For such cases two types of formula have been suggested : (i.) by Abegg (1) this may be written $\log D = \log D_0 - \alpha(\theta - 273)$, and (ii.) by Adams (2) $\log D = \log D_0 - n \cdot \log (\theta/273)$. In those cases in which we have tested these formulæ we have invariably found Abegg's quite as good as Adams's and in some cases better ; it is moreover simpler, and we therefore propose to express all our results in terms of it, using decadic logarithms.

Results.

1. *Benzene* *.—A specimen purified by Mr. R. W. Knight for use in some cryoscopic work was tested between 14° and 71° C.

Authors.	D_0.	$\alpha \times 10^3$.
L. and G.	2·2934	0·265
Cauwood and Turner (6)	2·2768	0·2865
Hasenöhrl (23)	2·1547	0·449
Negreano (41)	2·1939	0·526
E. H. L. Meyer (38)	2·2737	0·2985
Ratz (51)	2·2805	0·2935
Lange (34)	2·3033	0·330
Grützmacher (20)	2·3109	0·257
Graffunder (18)	2·3137	0·366
Stranathan (66)	2·3223	0·418
Tangl (67)	2·3326	0·403
Isnardi (27)	2·3516	0·458
Palaz (45)	2·3862	0·557
Schulze (59)	2·6139	2·253

* While this paper was in the press there appeared another by Hartshorn and Oliver (Proc. Roy. Soc. cxxiii. p. 664 (1929) in which they give 2·282 as the dielectric constant of benzene at 20° C.

Benzene (*cont.*).

Temp.	Authors.	Their D.	Our D.
12·7°	Landolt and Jahn (33).....	2·2074	2·276
13·4	,, ,, ,, ...	2·1977	2·275
14·2	Silberstein (61)	2·07	2·274
14·5	Landolt and Jahn (33).....	2·2221	2·273
15	Kerr (31)	2·28	2·2725
	Michaud and Balloul (40)	2·28	
	Saint-Antoine (54)	2·23	
16	Watson (75)	2·286	2·271
17	Siivola (60)	2·258	2·270
	Drude (10)	2·255	
	Veley (72)	2·27	
	Nernst (42)	2·255	
18	Turner (71)	2·288	2·268
	Errara (14)	2·285	
	Philip (47)	2·242	
19	Drude (10).....	2·26	2·267
19·6	Tomazewski (69)	2·218	2·266
20	Linebarger (36).....	2·249	2·266
	Philip and Haynes (48)	2·29	
25	Harris (22).....	2·2485	2·259
	Williams and Krchma (78)	2·283	
	Sayce and Briscoe (55)	2·23	
25·5	,, ,, (56)	2·239	2·258
80·15	Grimm and Patrick (19)	2·17	2·184

2. *Carbon tetrachloride.*—A good commercial sample tested between 15° and 71° C.

Authors.	D_0.	$\alpha \times 10^3$.
L. and G.	2·2655	0·461
Grützmacher (20)	2·2179	0·2755
Stranathan (66)	2·2610	0·399
Isnardi (27).....	2·3592	0·3175

Carbon tetrachloride (*cont.*).

Temp.	Authors.	Their D.	Our D.
12°·5	Veley (72)	2·049	2·236
17	Drude (10)	2·18	2·225
18	Turner (71)	2·246	2·2225
	Franke (16)	2·227	
	Schulz (59)	2·248	
20	Linebarger (36)	2·241	2·218
21·3	Bugarsky (4)	2·241	2·215
23	Grimm and Patrick (19)	2·2	2·211
25	Sayce and Briscoe (55)	2·20	2·206
	Williams and Krchma (78)	2·230	
	Harris (22)	2·1873	
76·7	Grimm and Patrick (19)	2·10	2·088

3. *Chloroform.*—A good commercial sample tested between 14° and 58° C.

Authors.	D_0.	$\alpha \times 10^3$.
L. and G.	5·372	1·736
Ratz (51)	5·1035	1·680
E. H. L. Meyer (38)	5·148	1·802
Tangl (67)	5·1865	1·460
Smyth and Morgan (64)	5·2145	1·7635
Cauwood and Turner (6)	5·310	1·768
Isnardi (27)	5·317	1·703
Grützmacher (20)	5·398	1·437

Temp.	Authors.	Their D.	Our D.
5°	Schulze (59)	5·646	5·2655
15	Joachim (30)	5·06	5·059
	Thwing (70)	3·95	
17	Drude (10)	4·95	5·019
	Kerr (31)	4·85	
17·8	Ortvay (44)	5·042	5·003
18	Turner (71)	5·2	4·999
	Walden (73)	4·95	
	Philip (47)	4·864	
	Nernst and Lerch (43)	5·1	

Chloroform (*cont.*).

Temp.	Authors.	Their D.	Our D.
20	Schulze (59)	4·857	4·959
	Linebarger (36)	5·132	
22	Nernst (42)	5·14	4·920
24	Carman (5)	5·6	4·8805
25	Williams (78)	4·770	4·851
	Harris (22)	4·642	
	Sayce and Briscoe (55)	4·79	
26	Schulze (59)	4·540	4·8415
61·2	Grimm and Patrick (78)	4·23	4·206
	Cauwood and Turner (6)	4·130	

4. *Mixture of Chloroform and Carbon tetrachloride* containing 38·80 per cent. by mass of chloroform.

Log D = log 3·2931 − 0·001015 (θ − 273). Interpolation of Grützmacher's values gives

log D = log 3·2435 − 0·000857 (θ—273).

5. *Methyl alcohol.*—A specimen kindly prepared for us by Sir H. B. Hartley. Investigated between 12° and 59° C.

$D_0 = 37·0635$, $\alpha = 0·002415$. Compare Abegg and Seitz (2), who found $D_0 = 34·735$, $\alpha = 0·002302$.

Temp.	Authors.	Their D.	Our D.
0°	Walden	34·9	37·06
13·4	Landolt and Jahn (33)	34·86	34·40
15	Thwing (70)	34·05	34·10
	Joachim (30)	36·17	
	Walden	36·17	
16	„	32·4	33·91
	Drude (10)	32·5	
17	„ „	33·2	33·72
18	Harrington (21)	33·78	33·53
	Rudolph (52)	31·5	
	Falkenberg (15)	33·0	
	Potapenko (49)	32·0	
24	Carman (5)	35·5	32·43

6. *Nitrobenzene.*—A good commercial sample dried and redistilled. Investigated between 15° and 70°C.

Authors.	D_0.	$\alpha \times 10^3$.
L. and G.	39·338	2·283
E. H L. Meyer (38)	36·235	2·019
Abegg and Seitz (2)	40·31	1·893
Lange (34)	42·175	2·485
Jezewski (29)	37·46	1·972

Temp.	Authors.	Their D.	Our D.
5°	Thwing (70)	32·19	36·355
	Kerr (31)	35·03	
	Joachim (30)	36·45	
16	Philip (47)	37·14	36·165
18	Errera (13)	35·67	35·785
	Turner (71)	36·45	35·785
20	Kerr (31)	33·91	35·41
25	Williams and Ogg (80)	36·10	34·495
	Harris (22)	34·093	
210·35	Grimm and Patrick (19)	15·61	12·99

7. *Nitromethane.*—Purified by Mr. C. P. Wright under the direction of Sir H. B. Hartley; boiling-point 101·15° C. Investigated between 12° and 92° C.

$$\text{Log D} = \log 40{\cdot}88 - 0{\cdot}00189\,(\theta - 273).$$

Comparison of Experimental Values in Condensers X, Y, and Z with those calculated by the above Formulæ for Nitromethane.

Temp.	λ.	X.	Y.	Z.	Calc.
12°	90·0	38·55	—	—	38·799
	76·6	—	38·64		
	80·34	—	38·87		
	137	—	38·68		
	131	—	39·02		
12·5	90·0	—	39·00	—	38·715
	102·7	38·72	—	38·52	

Nitromethane (*cont.*).

Temp.	λ.	X.	Y.	Z.	Calc.
12·9	108·2	38·67	—	38·45	38·647
	118	38·81	38·535	38·50	
	71·7	38·56	—	38·61	
14	96·2	38·35	38·48	38·34	38·446
16	193	38·25	38·22	38·13	38·129
	217·8	38·06	38·18	38·03	
	144	38·09	—	38·00	
	141	—	38·17		
	90·6	37·95	38·05	38·04	
17	115·6	38·26	38·14	38·27	37·964
22	96·2	37·03	37·245	37·08	37·147
		37·26	37·11	36·87	
29	96·2	35·935	35·695	35·81	36·033
40·4	96·2	33·98	34·00	33·985	34·288
48·75	96·2	33·00	32·89	32·86	35·064
61	96·2	31·285	31·29	31·14	31·349
71	96·2	30·06	30·01	29·81	30·014
81·5	96·2	28·77	28·77	28·56	28·673
91	96·2	27·67	27·75	27·43	27·512
			27·85	27·47	

Temp.	Authors.	Their D.	Our D.
15°	Thwing (70)...	56·36	38·24
19	Schlundt (58)	40·4	37·58
20	Walden (71).....	38·8	37·415
25	Grimm and Patrick (19)	39	36·61
101·7	„ „ „	27·75	26·22

8. *Water.*—As was mentioned earlier, it was not practical to find the temperature coefficient for water in condensers with plated electrodes ; but the results with cold water were in good accord with those of Kockel (32), Coolidge (9), Franke (16), Drude (10), and Ratz (51). These all agree substantially in giving the equation :

$$\log D = \log 87{\cdot}73 - 0{\cdot}0020095\,(\theta - 273).$$

How good is the agreement may be seen from the following table :—

Dielectric Constant of Water.

Temp.	Kockel.	Coolidge.	Franke.	Drude.	Ratz.	Calc.
0°	88·04	88·42	—	87·28	88·00	87·73
10	83·71	84·31	85·09	83·81	83·68	83·76
20	79·69	80·49	80·51	80·04	78·81	79·975
30	75·88	75·75	—	76·30	75·80	76·36
40	72·34	73·24	—	72·93	—	72·905
50	69·02	—	—	69·93	—	69·61
60	65·91	—	—	67·22	—	66·46
70	63·04	—	—	64·54	—	63·46
80	60·36	—	—	61·91	—	60·59
90	57·84	—	—	—	—	57·85
100	55·30	—	—	—	—	55·23

From measurements made at one temperature, only those which agree with the above formula need be quoted here.

Temp.	Authors.	Found.	Calc.
17°	Palmer (46)	81·40	81·09
	Weichmann (76)	80·28	
	Colley (8)	80·26	
	Heerwagen (25)	80·88	
	Holborn (26)	81·51	
	Wildermuth (77)	80·5	
	Abegg (1)	80·84	
17·5	Nernst (42)	80·3	80·905
18	Nernst and Lerch (43)	81·7	80·72
	Sack (53)	80·85	
	Ercera (14)	81·02	
	Turner (71)	81·07	
18·7	Cohn and Zeeman (7)	80·19	80·455
19	Mazotto (37)	81·00	80·345
20·75	Heerwagen (25)	79·56	79·70
21·15	Cohn and Zeeman (7)	78·88	79·54
22·2	„ „ „	79·8	79·165

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CXIII. *The Rare Earths associated with Uraninites.*

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THE fact is well known that seldom are radioactive minerals free from rare earths, or rare earth minerals lacking in an appreciable content of uranium or thorium. Chemically, both uranium (uranous) and thorium bear close resemblances to the rare earths ; and this similarity might be thought sufficient to account for their association with the cerium and yttrium groups of elements. Our knowledge, however, is very inadequate, and the present investigation was undertaken with the object of studying more closely than has been done heretofore the nature of the rare earths associated with minerals consisting essentially of uranium oxides.

Very complete analyses of uraninites from a large number of different sources were made about 1890 by Hillebrand (Amer. Journ. Sci. xl. p. 384, 1890 ; xlii. p. 390, 1891) on the material then available. Most of these contained several per cent. of thoria and from 1 to 10 per cent. of rare earths. His analyses show, in all cases where his rare-earth group was divided, that the yttrium subgroup (*i. e.*, yttrium and atomic numbers 66 to 71, or the more feebly basic earths, and those with highest atomic weight) represented a considerable proportion, often much the larger proportion, of the earths present.

If all the analyses now available are examined it will be noticed that the older uraninites are richer in thorium and the rare earths than the younger, though there is no apparent proportionality between the rare earth and lead content. The result is sufficiently striking in the case of the rare earths to warrant an investigation as to whether any evidence can be deduced to show that there has been a growth of the earths in the course of time. In many cases it is obvious that the rare earth is present in such a large proportion as to make fairly certain that it was an original constituent of the mineral, and so the minerals investigated should be those having a minimum rather than a maximum of rare earth.

Isolation of the Rare-Earth Group.

The general procedure was to attack the powdered mineral with hot nitric acid and evaporate to dryness. The

* Communicated by Prof. Fredk. Soddy, F.R.S.

residue was taken up in water and any insoluble remainder removed. Lead and radium were then precipitated as sulphates, and following this the H_2S precipitate was removed. Excess of hydrofluoric acid was then added. This caused precipitation of thorium and the rare earths. The thorium was best removed by adding to a dilute boiling solution of the mixed chlorides a sufficiency of sodium thiosulphate, causing a basic thorium thiosulphate to precipitate. The earths were finally obtained pure by repeated precipitations as oxalates and ignition.

TABLE I. Uraninites examined.

No.	Locality.	Rare-earth content.	Age*.
		Per cent.	
1.	Joachimstal, Czecho-Slovakia.	·0	205×10^6 years.
2.	Katanga, Belgian Congo.	·15	575
3.	S. India.	·7	900
4.	Morogoro, Tanganyika Territory.	·1	640
5.	Cornwall.	·17	220
6.	Norway.	1·0	900

No. 1. The actual pitchblende was not examined, but a rare-earth residue obtained from the radium factory. The analyses on record show no rare-earth content, but some is found on large-scale work.

No. 2. The earth from 1 kg. of average ore was available for examination.

No. 3. The specimen was about half black pitchblende and about half weathered to a soft yellow earth.

No. 4. The sample was a fine compact black pitchblende with which was some yellow Rutherfordine and a little mica.

No. 5. The pitchblende contained copper and arsenical pyrites, galena, and much titanium.

No. 6. The material was crystalline Bröggerite of high degree of purity.

Methods of Examination.

The arc spectrum of the oxides and the absorption spectrum of a chloride solution were examined in each case.

Part of the work was done on a Féry spectrograph and part with a large Littrow spectrograph, the region 2500 to

* From Holmes, 'The Age of the Earth' (Ernest Benn, Ltd., 1927).

3500 A.U. only being photographed with the latter instrument in the examination of the arc spectra. Spectrograms from the Féry instrument were projected with a 12-5 times enlargement against a scale of wave-lengths ruled to suit. The error in reading the wave-lengths below 3500 Å.U. did not amount to more than ·1 or ·2 Å.U. *.

Photos from the larger instrument were projected so as to obtain the same dispersion, and comparison with prints from the smaller instrument could then be made directly. It was not difficult to identify almost all the lines with one or other of the rare-earth elements. Some of the rare earths give easily identified lines, even when present in very small quantity. These, fortunately, are the elements which usually cannot be identified by their absorption spectra, viz., Yt, Yb, Eu, Gd, La, Lu, Sc. The elements Dy, Ho, Tm, Er, Sm, Tb, and Ce give less prominent lines, whilst Pr and Nd give no lines, at any rate in the ultra-violet, which enable them to be distinguished with certainty in a mixture unless they form a large proportion of the whole. They may, on the other hand, be detected very delicately by their absorption spectra.

A chloride solution of each earth was prepared by dissolving the oxide in hydrochloric acid and making up the solution to a volume which represented ·4 gm. E_2O_3 per c.c. Absorption photographs were taken through 1 cm. thicknesses of this solution, using a source of continuous emission. In some cases a further photograph was taken, using a 5-cm. layer. Each of the coloured earths possesses at least one band fairly well distinct from strong bands of all other elements, which made it possible to identify it in the crude mixture.

Results.

An attempt was made to obtain an approximate estimate of the amount of each earth present by selecting a weak isolated band, and from the data of other workers determining what concentration its presence indicated for that earth in the solution. The bands found useful and the results arrived at are shown in Table II. The 40-per-cent. oxide-chloride solution employed probably represented a strength of about 8 times normal. The estimate is for Joachimstal earths, and for comparison the amount of the various earths

* See O. Free, Phil. Mag. lx. p. 950 (1926), for description of this method.

found on actual fractionation is also given as accurately as possible.

In the material which was fractionated, lanthanum and cerium had been removed previously.

An approximate estimate of the actual amount of rare earth present in the six samples of uraninite is found in Table I. "Uraninites examined" (p. 1006). It will be seen that the two oldest samples contain considerably higher amounts than the others. These two (Norwegian Bröggerite and Indian pitchblende) were also the only ones to contain appreciable quantities of thorium. The former held 1 per cent. and the latter ·7 per cent. The next highest thorium-content was in the Cornish pitchblende, and this, it will be seen, though young, had the third greatest rare-e content.

TABLE II.

Element.	Band.	Amt. in 8N solution.	Per cent. on fractionation.
Praseodymium.	4441	N/2	4
Neodymium.	6250	N	16
Samarium.	4070	N/2	6
Europium.	3950	N/5	2
Gadolinium and terbium.	—	—	7
Dysprosium.	3865	N/2	4 ?
Holmium.	6430	N/10	1 ?
Erbium.	6536	N/3	} 56
Yttrium.	—	—	
Ytterbium.	—	—	4

Scandium.—This earth was found to constitute at least 10 per cent. of the rare earth present in Katanga pitchblende. The element accompanies thorium in the thiosulphate method of separation from the rare earths, and was detected spectroscopically in the thorium from Indian pitchblende on adding to its solution ammonia and ammonium tartrate and boiling. Only 2 milligrams, however, were obtained. None was thus separable in the other cases, but in every case some of the very highly sensitive lines were detectable in the arc spectrum. They were strongest in the Morogoro earth and seen next best in Bröggerite.

Europium.—The distribution of this element was found to be of considerable interest. It may be detected by its arc spectrum when only the minutest traces are present, and

ordinarily, with the exception of illinium, it is least abundant of the rare-earth elements. It was found to be virtually absent in the Indian pitchblende, and in the Bröggerite there was only a very minute quantity. On the other hand, the Katanga and Joachimstal pitchblendes must be among the richest sources of the element yet found. Urban (*J. chim. phys.* iv. p. 232, 1906) has already remarked upon its abundance in pitchblende, presumably from Joachimstal, estimating it as greater than the gadolinium- and almost as great as the samarium-content. Whilst the present work does not quite bear out this proportionality, it has been found by actual fractionation of 300 grams of rare earths from Joachimstal residues that the content must approach 2 per cent. in the crude mixture. This may be compared with a content in monazite said not to exceed ·002 per cent. The europium absorption band at 3950 A.U. was observed in a 1-cm. layer of concentrated solution of the mixed earths, and from its strength a rather higher, but not dissimilar, estimate of its abundance was arrived at. The amount present in the Katanga earths appears from the absorption spectrum to be even greater, and the content in Morogoro earth is probably not widely different, though rather less than in the material from Joachimstal.

With regard to the other earths, it may be stated that the Cornish material was richest in cerium and the cerium group. Lanthanum was not present to any appreciable extent in Morogoro and Bröggerite earths, and the amount in the Indian earths was small. These three materials contained the highest proportions of yttrium. The Morogoro product in particular gave less indication of coloured earths than the others, the neodymium and praseodymium absorption bands being very weak. The oxides themselves were pale in colour. The amount of samaria in Joachimstal and Katanga earths was unusually high. In the Joachimstal material which was fractionated the amount was found to be 4 to 5 per cent., or equal to about one-third of the neodymium present. The proportions of the earths in this mixture, however, had been disturbed from the original by the extraction from them of the actinium and some of the most basic earths, and of ionium and some of the least basic earths. The remainder which was submitted to fractionation had consequently probably gained a little in richness in earths occupying a central position in the usual serial order of the elements. The estimate is also made on the cerium-free material, and cerium amounted to nearly 20 per cent. of the earth before its removal.

Gadolinium arc lines could be detected in all cases with ease, but owing to their sensitivity they do not afford much evidence of the amount present. The general absorption of the earths masked the absorption bands of gadolinium, which all lie in the ultra-violet, so that no use could be made of them in arriving at an estimate of the abundance. In the Joachimstal material, on fractionation about 6 per cent. was isolated. Terbium appears to be abundant in the Indian earths and scarce in the Katanga. This, it may be remarked, is just the reverse of what is found in the case of europium. The amounts present, however, are small and the evidence scanty. Dysprosium and holmium are relatively most abundant in Indian and Bröggerite earths. Of the remaining earths there is little that can be recorded. Yttrium with a little erbium constitutes at least 50 per cent. of the 300 grams of Joachimstal earths that were fractionated.

It is instructive to compare the above results with the work of Hauser and Wirth (*Ber.* xlii. p. 4443, 1909). They have made a study of the earths occurring in euxenites (yttrium columbo-titanites) and polycrases (yttrium columbo-tantalates), and find praseodymium and samarium to increase in abundance with the amount of titanic acid. Also thorium and titanium occur together, or not at all, in the columbates which they examined. The earths from Joachimstal, Katanga, and Morogoro appear to resemble extreme examples of the tantalic acid type. In the other three earths which contained either considerable titanium or thorium, the type corresponding, according to the views of Hauser and Wirth, appears dominant; and most markedly is this so in the Indian earths, where the thorium content is highest. No actual information with regard to the tantalum-content of the different minerals was obtained.

The mineral samarskite is said to be the best source of europium among the ordinarily available rare-earth minerals. This is a columbo-tantalate of rare earths with 10 to 15 per cent. of uranium oxides and very little thorium. Bearing in mind what has been said previously with regard to europium, it would appear to be a general rule that uranium and europium associate together in nature, but that thorium and europium do not.

Conclusions.—Enough has been said to make it clear that the earths of pitchblende show no features in common more than will be found amongst almost any six rare-earth samples taken at random from different minerals. It seems possible that the earths are not actually part of the uraninite in all cases, but are in reality derived from some associated mineral

such as samarskite. Thus Hauser (*Ber.* xliii. p. 417, 1910) has described a mineral, plumboniobite, which is found together with the Morogoro pitchblende at Morogoro, and which is very rich in samarium and gadolinium. W. Markwald (*Zentr. Min. Geol.* p. 761, 1906) found 2 per cent. of rare earth in his analysis of Morogoro pitchblende—a much greater amount than the author has found in his very pure sample. However, the earths separated in the present investigation were remarkable, like the earths from Hauser's plumboniobite, in their lack of lanthanum, cerium, and didymium ; and the conclusion seems justifiable that in this instance the rare earth is an intimate associate rather than a genuine constituent of the pitchblende.

The rare earth in pitchblende is due to imperfections in the chemical or physical separations which have taken place during magmatic differentiation, or subsequent segregations. The greater amount of rare earth in very old uraninites may probably be accounted for as being due to a greater turbulence in the magma and greater volcanic acitvity 10^9 years ago than in more recent times.

In conclusion, I wish to acknowledge my debt of gratitude to Prof. Soddy for laboratory facilities provided during a large part of this work, and for his interest in it. It was undertaken at his suggestion, and largely made possible by the use of materials placed at my disposal by him.

CXIV. *The Acoustic Performance of a Vibrating Rigid Disk driven by a Coil situated in a Radial Magnetic Field* *. *By* N. W. McLachlan, *D.Sc.*, *M.I.E.E.*, *F.Inst.P.* †

Synopsis.

1. Analysis of System without Elastic Constraint.
2. „ „ with „ „
3. Transient Solutions.
4. Acoustic Pressure on Disk and Power radiated.

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* This paper, together with the analysis of the pressure distribution round the disk, to which reference is made herein (Proc. Roy. Soc. A, vol. cxxii. p. 604, 1929), was compiled in May 1926. Its publication has unfortunately been delayed, due to causes over which the author had no control. It was received by the Editor on March 18, 1929.

† Communicated by the Author.

5. Accession to Inertia due to Motion of Disk.
6. Simple Formulæ for Air-pressure and Power radiated.
7. Illustration of Analytical Expressions.
8. Current in Moving Coil.
9. Reactance of Moving Coil.
10. Axial Pressure.
11. Power radiated as Sound.
12. Transients.

Abstract.

The object of this paper is to examine analytically the performance of an arrangement akin to the type of loud speaker used for acoustic reproduction in which the driving agent is a circular coil situated in a strong radial magnetic field.

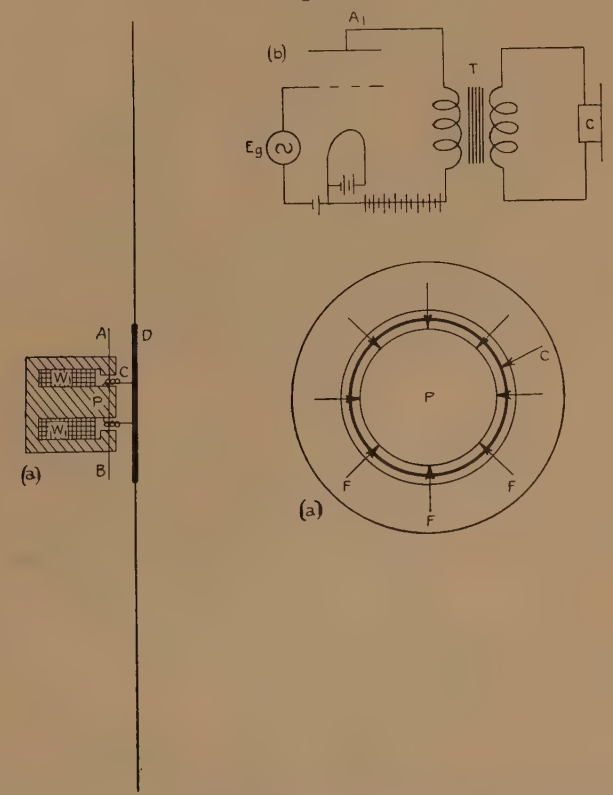
Accordingly the paper deals with the acoustic performance of a rigid disk, supported at its periphery and driven by a concentric circular coil situated in a radial magnetic field of constant value. Alternating current passed through the coil (which is connected in the anode circuit of a thermionic valve) causes the disk to vibrate axially. The simultaneous differential equations associated with the mechanical and electrical aspects of the problem are solved for the steady and the transient state, with and without elastic constraint at the periphery. Expressions are obtained for the acoustic radiation resistance, the acoustic power radiated, and the current in the moving coil. It is shown that the e.m.f. induced in the coil, due to its motion in the magnetic field, is concomitant with a capacity reactance in quadrature with the acoustic radiation resistance. By virtue of this and the inductance of the coil, the system has an electromechanical resonance frequency. If the damping is adequately small the mechanical system will execute oscillations in the absence of elastic constraint. Electrical circuit diagrams equivalent to the mechanical and electrical systems combined are given for the constrained and unconstrained conditions of the disk. These facilitate the study of transients.

The analysis is illustrated by curves showing the coil current, acoustic output, and axial pressure for three different disks. It is shown that, under set conditions, there is a certain size of disk for which the output is a maximum. A curve is also given by the aid of which the accession to inertia due to the divergence of the waves propagated by the disk can be evaluated.

(1) *Analysis of System without Elastic Constraint.*

THE essential components of the device to be analysed are shown in fig. 1. The diaphragm is situated in a plane wall of infinite extent so that there is no interference between the two sides. The disk is driven axially to and fro

Fig. 1.



(*a*) Illustrating arrangement of circular coil in radial magnetic field due to electromagnet.

On the right is an enlarged section at the plane AB. P = Central pin. C = Coil. D = Rigid disk. F = Radial magnetic field. W_1W_1 = Field winding.

(*b*) Showing valve-circuit connexions for supplying electrical energy to coil. A simplified equivalent circuit is given in fig. 2.

A_1 = Thermionic valve. E_g = sine-wave voltage to grid of valve (maximum). T = 1/1 transformer with zero leakage and self-capacity which gives the same alternating current performance as when the coil is connected in the valve circuit. C = Coil in magnetic field.

by means of a circular coil immersed in a strong radial magnetic field caused by a permanent magnet or an electromagnet. Alternating current of variable frequency is obtained in the anode circuit of the valve A_1 by applying a constant e.m.f. of sine-wave form to its grid and filament. Since the transformer T is assumed to be perfect, the alternating current passing through the primary is equal to that through the secondary. Moreover, so far as alternating current is concerned, the moving coil can be considered to be in the anode circuit of the valve. Thus the coil drives the disk, which consequently emits sound from both sides. In the analysis it will be assumed: (1) that the diaphragm is a perfectly rigid disk *; (2) that the restraint due to the suspension is negligible; (3) there is no loss due to eddy currents in the air; (4) the magnet etc. does not impede the sound-waves; (5) there is no mutual electromagnetic or electrostatic action between the moving coil and the magnet coil, or the permanent magnet, whichever is used; (6) there is no mutual acoustic action between the device and its surroundings, *i. e.*, it operates in undisturbed air.

The differential equations for the system are as follows:—

$$m\mathrm{D}^2x + \mathrm{B}\mathrm{D}x = \mathrm{C}i, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

m { = mass of disk and coil + equivalent mass of air on both sides of the disk.
= $\mathrm{M} + \mathrm{M}_1$ = effective mass of moving system.

B = a factor depending on the alternating pressure due to sound-waves on both sides of the disk †.

C { = force on moving coil per unit current (absolute).
= total flux interlinkages of field and coil.

x = axial displacement of disk.

$$\mathrm{L}\mathrm{D}i + \mathrm{R}i + \mathrm{C}\mathrm{D}x = e, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

L = total inductance in coil circuit.

R = total resistance in coil circuit (including valve).

E = voltage applied to coil circuit (maximum value).

Instantaneous $e = \mathrm{E} \sin(\omega t + \alpha)$.

* Velocity of propagation of energy down disk is infinite, so that it moves as a whole at all frequencies.

† For analytical purposes this factor may be assumed to include additional linear damping, *e. g.*, fluid friction due to the viscosity of the medium. In the work herein the viscosity component has been omitted because its value is unknown.

Solving (1) and (2) :

From (1) $$i = \frac{1}{C}(mD^2x + BDx).$$

Substituting for i in (2),

$$\frac{1}{C}(LD + R)(mD^2x + BDx) + CDx = e$$

or $$Dx = \frac{eC}{[mLD^2 + (mR + BL)D + BR^2 + C^2]}, \quad . \quad (3)$$

where $D = j\omega$ for a steady sine wave.

Substituting for D in (3):

Velocity of disk =

$$Dx = \frac{eC}{\{(BR + C^2 - \omega^2 mL)^2 + \omega^2(mR + BL)^2\}^{\frac{1}{2}}}. \quad . \quad (4)$$

and the acoustic pressure on the disk at any instant $= BDx$.

The acoustic power factor may be defined as

Acoustic pressure/Driving force

or $$\cos\theta = \frac{B}{(B^2 + \omega^2 m^2)^{\frac{1}{2}}}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the load component BDx is in quadrature with the inertia component mD^2x.

Taking, now, the electrical side of the problem, we get from (1) and (2), solving for i,

$$Dx = \frac{1}{C}[e - i(R + LD)],$$

or $$D^2x = \frac{1}{C}[De + i(RD + LD^2)]. \quad . \quad . \quad . \quad (6)$$

Substituting from (6) in (1), we get

$$m[De - i(RD + LD^2)] + B[e - i(R + LD)] = C^2 i;$$

$$\therefore \quad i\{C^2 + BR + (BL + mR)D + mLD^2\} = mDe + Be$$

$$= e(mD + B). \quad . \quad (7)$$

Substituting $D = j\omega$, we have

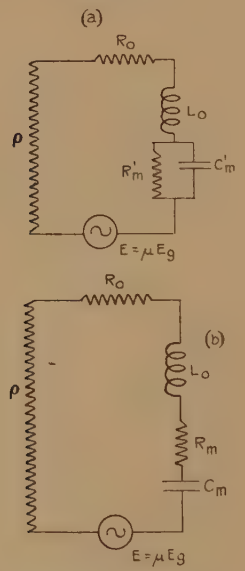
$$i = \frac{e(B^2 + \omega^2 m^2)^{\frac{1}{2}}}{\{(C^2 + BR - \omega^2 mL)^2 + \omega^2(BL + mR)^2\}^{\frac{1}{2}}}. \quad . \quad (8)$$

The equivalent circuit for the coil is shown in fig. 2 (*a*). Here we have the internal alternating current valve resistance ρ in series with the alternating current resistance R_0 of the coil, when immovable ; the inductance of the coil, when

immovable, L_0; and a fictitious radiation resistance R_m' shunted by a fictitious motional condenser C_m'. For simplicity in manipulation the parallel circuit R_m', C_m' can be replaced by a series arrangement, as shown in fig. 2 (*b*). The values of R_m' and C_m' vary with the frequency, They are, of course, due to the back e.m.f. induced in the coil by the virtue of its motion in the magnetic field.

The power radiated as sound can be written $I^2_{r.m.s.} R_m$, where R_m is the effective motional or acoustic radiation resistance, as in fig. 2 (*b*).

Fig. 2.



μ = Amplification factor of valve.
E_g = Voltage change on grid of valve (maximum).
E = Fictitious alternator corresponding to voltage change on anode of valve.
ρ = Internal A.C. resistance of thermionic valve.
R_0 = Effective resistance ot coil when at rest.
L_0 = Effective inductance of coil when at rest.
$R_m' = C^2/B$ = Equivalent acoustic radiation resistance. } Parallel
$C_m' = m/C^2$ = Equivalent motional capacity. } arrangement.
R_m = Acoustic radiation resistance. } Series
C_m = Motional capacity. } arrangement.

Inserting the value of $I_{r.m.s.}$ from (8), we get

$$\text{Radiated power} = \frac{E^2_{r.m.s.}(B^2 + \omega^2 m^2) R_m}{Q}, \quad . \quad . \quad (9)$$

where Q is the square of the denominator of (8).

Also

$$\text{Radiated power} = \text{Pressure} \times \text{Velocity of disk},$$
$$= BD\dot{x}D\dot{x} \text{ (the velocity being r.m.s. value)},$$
$$= \frac{BC^2E^2_{\text{r.m.s.}}}{Q} \text{ from (4)}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Equating (9) and (10), we get

$$R_m = \frac{BC^2}{(B^2+\omega^2m^2)}$$
$$= \frac{C^2\cos^2\theta}{B} \text{ from (7)}. \quad . \quad . \quad . \quad (11)$$

The two components of the back e.m.f. due to the motion of the coil are in quadrature. Moreover, it can be shown that

$$\tan\theta = \text{reactance/resistance}$$
$$= \frac{1}{\omega C_m R_m}$$

or
$$C_m = \frac{1}{\omega R_m \tan\theta}.$$

Substituting the value of R_m from (11), we get

$$C_m = \frac{m}{C^2\sin^2\theta} = \frac{m}{C^2(1-\cos^2\theta)}. \quad . \quad . \quad . \quad (12)$$

Now, the current in the moving coil is (see fig. 2 (*b*))

$$\frac{\text{Voltage}}{\text{Impedance}} = \frac{E}{Z}$$

or
$$I = \frac{E}{\left[(R+R_m)^2 + \left(\omega L - \frac{1}{\omega C_m}\right)^2\right]^{\frac{1}{2}}}. \quad . \quad . \quad (13)$$

The acoustic pressure = Force due to current in coil × Acoustic power factor = $CI\cos\theta$

$$= \frac{EC\cos\theta}{Z}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

It can be shown that when the condenser and resistance are in parallel

$$R_m' = \frac{C^2}{B} \quad \text{and} \quad C_m' = \frac{m}{C^2}.$$

Thus, as f increases, both R_m' and C_m' decrease. These formulæ comply with equation (6), and are therefore valid

for the transient and for the steady state. By means of fig. 2 *a* it is possible to study the effect of transients. If we imagine a battery to be suddenly switched in to replace the alternator in fig. 1, a voltage will be applied to the circuit rising from zero to E instantaneously. This can be resolved into an infinite spectrum of frequencies. The low frequencies will be impeded by C_m', although part will be by-passed by R_m'. The high frequencies will be by-passed by C_m' but impeded by L_0. Thus there will be a definite phase-shift of the high- and low-frequency components of the impulse. The attenuation of the former by L_0 will reduce the rate of rise of the current so that the impulse profile will be rounded. Hence, to reduce distortion with transients of steep wave front, *e. g.*, piano, gun-firing, the coil inductance should be small. There is also the transient when the battery is replaced by a short-circuit. In the ideal case the current in the system would cease immediately. But the electromagnetic energy $\frac{1}{2}Li^2$ and the electrostatic energy $\frac{1}{2}C_m'v^2$ have to be dissipated. Since this occupies a definite time-interval, there is a rounding of the transient. From a physical standpoint the charge to C_m' is represented by the mechanical moving system gradually increasing in velocity. The by-passing effect of R_m' is the damping effect of the air on the moving disk. As the velocity increases, so also does the back e.m.f., thereby reducing the coil current. The charging current of C_m' falls exponentially.

When the battery is replaced by a short-circuit, the kinetic energy of the mechanical system is expended in keeping the disk in motion against the air and the electromagnetic damping. This is represented by the discharge of C_m' through R_m' and the remainder of the circuit. The disk comes to rest exponentially.

Coming to the steady state, this is more readily seen by the aid of fig. 2 (*b*). The condenser C_m means increased impedance at low frequencies. There is electromechanical resonance in the middle register, the current being a maximum and falling away on either side. Hence the force acting on the coil varies with the frequency. To reduce the variation in impedance it is essential to use a power valve whose internal resistance is large compared with the capacitive and inductive reactances.

(2) *Analysis of System with Elastic Constraint.*

This case includes not only a coil drive in which the rigid disk is supported elastically at the periphery, but also a rigid disk freely supported at the periphery and driven by

an electromagnetically operated reed or other elastic member at the centre.

The equations are now

$$mD^2x + BDx + k_1x = Ci, \quad . \quad . \quad . \quad . \quad (15)$$

$$LDi + Ri + CDx = e, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

which, on solution for the steady state, yield

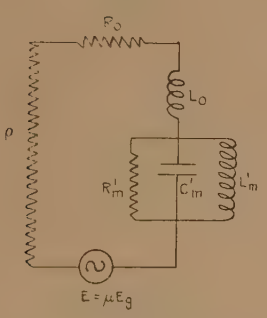
$$Dx = \frac{e\omega C}{\{[\omega^2(k_1L + BR + C^2) - \omega^2 mL]^2 + [k_1R - \omega^2(BL + Rm)]^2\}^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad (17)$$

and

$$i = \frac{e[(k_1 - \omega^2 m)^2 + \omega^2 B^2]^{\frac{1}{2}}}{Q_1}, \quad . \quad . \quad . \quad . \quad (18)$$

where Q_1 is the denominator of (17) and k_1 the coefficient of restitution.

Fig. 3.



$R_m' = C^2/B.$ $\quad$ $L_m' = C^2/k_1.$

$C_m' = m/C^2.$ $\quad$ $k_1 =$ coefficient of restitutio .

See fig. 2 for meaning of other symbols.

The equivalent electrical circuit for this case is shown in fig. 3. Here we have a circuit identical with that for the coil drive without constraint, except that now there is an inductance $L_m' = C^2/k_1$ in parallel with R_m' and C_m', which have the same values as before. Here we have two possibilities of resonance, viz., L_0 with C_m' and L_m' with C_m'. The resonances are modified, of course, by R_m'. The first, which corresponds to the electromechanical resonance, is still further modified by L_m', and the second, which corresponds to the resonance of the elastic constraint, is modified by L_0.

The problem of transients in this case can be analysed in the same manner as that indicated in connexion with fig. 2 (*b*). For both figs. 2 (*b*) and 3 the damping for the $L_0\ C_m'$ combination is such that oscillation does not occur, but for the $L_m'\ C_m'$ case, unless P, R_0 and R_m' are sufficiently small, an impulse will call forth the natural note of the system. This latter condition must be avoided in practical work.

(3) *Transient Solution.*

For the transient solution of the problem, we shall neglect the damping due to acoustic radiation, since it is small compared with that due to the motion of the coil in the magnetic field. We shall consider the question of the decay of the oscillations when the operating current in the coil ceases. So far as the time constant of the coil at rest is concerned, this is usually quite low enough to be neglected by comparison. It is generally less than 10^{-4} second.

The equations are now

$$m\mathrm{D}^2x = \mathrm{C}i. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$\mathrm{L}\mathrm{D}i + \mathrm{R}i + \mathrm{C}\mathrm{D}x = 0. \quad . \quad . \quad . \quad . \quad (20)$$

Hence, substituting from (19) in (20),

$$\left[\mathrm{D}^3 + \frac{\mathrm{R}}{\mathrm{L}}\mathrm{D}^2 + \frac{\mathrm{C}^2}{m\mathrm{L}}\right]x = 0\ ; \quad . \quad . \quad . \quad . \quad (21)$$

$$\therefore \quad \mathrm{D}x = 0, \quad i.e., \quad x = \mathrm{X}_1 \text{ a constant} \quad . \quad (22)$$

and

$$\left(\mathrm{D}^2 + \frac{\mathrm{R}}{\mathrm{L}}\mathrm{D} + \frac{\mathrm{C}^2}{m\mathrm{L}}\right)x = 0. \quad . \quad . \quad . \quad . \quad (23)$$

There are the usual three solutions for the aperiodic, critical, and oscillatory cases of (21).

Aperiodic.

$$x = \mathrm{A}e^{\lambda_1 t} + \mathrm{B}e^{\lambda_2 t} + \mathrm{X}_1, \quad . \quad . \quad . \quad . \quad (24)$$

where

$$\left.\begin{matrix}\lambda_1 \\ \lambda_2\end{matrix}\right\} = -\frac{\mathrm{R}}{2\mathrm{L}} \pm \left[\frac{\mathrm{R}^2}{4\mathrm{L}^2} - \frac{\mathrm{C}^2}{m\mathrm{L}}\right]^{\frac{1}{2}} \quad \text{and} \quad \frac{\mathrm{C}^2}{m\mathrm{L}} < \frac{\mathrm{R}^2}{4\mathrm{L}^2};$$

Critical.

$$x = e^{-\frac{\mathrm{R}t}{2\mathrm{L}}}(\mathrm{A}t + \mathrm{B}) + \mathrm{X}_1, \quad . \quad . \quad . \quad . \quad (25)$$

where

$$\frac{\mathrm{C}^2}{m\mathrm{L}} = \frac{\mathrm{R}^2}{4\mathrm{L}^2}.$$

Oscillatory.

$$z = e^{-\frac{Rt}{2L}}(A\cos\beta t + B\sin\beta t) + X_1, \quad . \quad . \quad (26)$$

where

$$\beta = \left[\frac{C^2}{mL} - \frac{R^2}{4L^2}\right]^{\frac{1}{2}} \quad \text{and} \quad \frac{C^2}{mL} > \frac{R^2}{4L^2}.$$

In practice, where a conical diaphragm would be used in place of the rigid disk, the motion is usually aperiodic. The oscillatory case, however, is of interest, for it shows that oscillations can occur without mechanical constraint. The explanation is simply that the kinetic energy $\frac{1}{2}mv^2$ is stored and re-stored as electrokinetic energy $\frac{1}{2}Li^2$, *i. e.*, the coil is brought to rest by generating an opposing current due to its cutting the magnetic field. This current then sets the disk and coil in motion in the opposite direction, the damping being the same as that of the coil at rest, since we agreed to neglect the motional resistance. It is obvious that this condition must be avoided in practice, or every transient would start and stop to the accompaniment of the natural electromechanical frequency.

Solving the aperiodic case, we get the linear velocity

$$Dx = \frac{v}{\lambda_1 - \lambda_2}\{\lambda_1 e^{\lambda_2 t} - \lambda_2 e^{\lambda_1 t}\}, \quad . \quad . \quad . \quad (27)$$

where v is the velocity of the disk when the driving force ceases.

The time taken to come to rest under the usual hypothesis is infinite. However, in our case it is only necessary to find the time taken for the velocity to be reduced to a certain percentage of its maximum value, *e. g.*, 10 per cent.

So far as the critical case is concerned, the linear velocity is

$$Dx = ve^{-\frac{Rt}{2L}}\left(\frac{Rt}{2L} + 1\right). \quad . \quad . \quad . \quad . \quad (28)$$

In the oscillatory case we have the natural frequency, as

$$f = \frac{1}{2\pi}\left[\frac{C^2}{mL} - \frac{R^2}{4L^2}\right]^{\frac{1}{2}} = \frac{1}{2\pi}\left[\frac{1}{LC_m} - \frac{R^2}{4L^2}\right], \quad . \quad (29)$$

and the linear velocity is

$$Dx\, ve^{-\frac{Rt}{2L}}\left\{\cos\beta t - \frac{\alpha}{\beta}\sin\beta t\right\}. \quad . \quad . \quad . \quad (30)$$

(4) *Acoustic Pressure on Disk and Power radiated.*

The pressure on a rigid circular disk vibrating in an equal circular aperture situated in a rigid plane plate of infinite extent has been treated analytically by the late Lord Rayleigh*. He assumed that there was neither eddy current nor other source of loss, and that the amplitude of motion of the disk on its axis is insufficient to affect appreciably the wave progagation in the neighbourhood of the disk. The total pressure on the disk is the vector sum of two components in quadrature: (*a*) the acoustic pressure in phase with the velocity, (*b*) an inertia component 90° out of phase with the velocity which arises due to divergence of waves from the disk. The latter is in effect a mass to be added to the disk, and is treated in the next section. The result given by Rayleigh is as follows :—

$$\text{Acoustic pressure due to radiation of sound-waves from } \textit{both} \text{ sides of the disk is } P_{r.m.s.} \begin{cases} = 2\rho_d A c \left[1 - \dfrac{J_1(2ka)}{ka}\right] \dot{X}, \\ = B\dot{X}, \quad . \quad . \quad . \quad . \end{cases} \quad (31)$$

where

$$B = 2\rho_d A c G \text{ and } G = \left[1 - \frac{J_1(2ka)}{ka}\right].$$

ρ_d = density of air (in gms. per cm.^{3}).

A = area of disk (in cm.^{2}).

c = velocity of sound (cm. per sec.).

$k = \omega/c$.

a = radius of disk (in cm.).

$\dot{X}$ = r.m.s. axial velocity of disk (cm. per sec.).

$y = x \tan \omega t$ (instantaneous value).

The power radiated is

$$W = \text{pressure} \times \text{axial velocity (r.m.s. values)},$$

$$= B\dot{X}^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

For a simple harmonic motion apart from phase, $\dot{X} = \omega Y$, where Y is an r.m.s. value.

Thus

$$P_{r.m.s.} = B\omega Y \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

and

$$W = B\omega^2 Y^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

* 'Sound,' ii. p. 162.

Now,

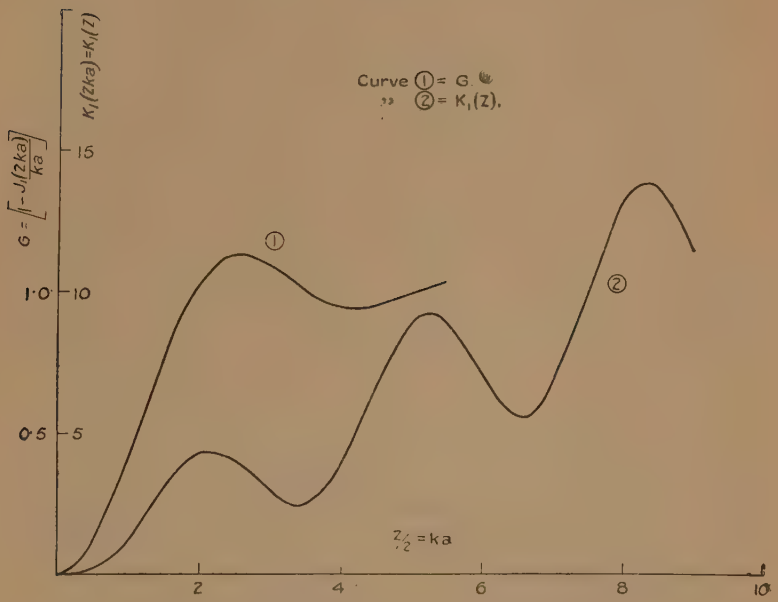
$$G = \left[1 - \frac{J_1(2ka)}{ka}\right] = \frac{k^2a^2}{1.2} - \frac{k^4a^4}{1.2^2.3} + \frac{k^6a^6}{1.2^2.3^2.4} \text{ etc.},$$

so that when ka is small, G is approximately equal to

$$\frac{k^2a^2}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

As ka increases, G gradually increases due to decrease in the term $\frac{J_1(2ka)}{ka}$. When $ka = 1{\cdot}9$, G becomes unity, and

Fig. 4.



Curves illustrating the functions G and K_1 (z).

as ka is increased, G ultimately oscillates about this value, as shown in fig. 4. Interpreted in the physical sense, when the frequency or the diaphragm is large enough to violate the relationship $G = k^2a^2/2$ appreciably, interference of the radiation from various parts of the disk occurs in space, *i. e.*, there is a transition from spherical wave propagation. As the frequency or the diameter is still further increased, the focussing of the sound due to interference gradually becomes more pronounced until $G = 1$, after which the interference

causes the pressure on the disk to oscillate from lower to higher values, *i.e.*, the wave propagation is sensibly plane. Up to the point $ka=0{\cdot}3$, the value of G is substantially $k^2a^2/2$, whilst for $ka=0{\cdot}5$ the error is only $+5$ per cent., which is small so far as aural appreciation is concerned. Thus, for a disk 10 cm. radius, focussing in air at N.T.P. would begin when $f=250\sim$. For a disk 5 cm. radius the frequency would be $500\sim$, *i.e.*, the frequency at which focussing begins is inversely proportional to the diameter of the disk. Since focussing depends upon the velocity of propagation of sound, it is clear that it will commence at a higher frequency in a gas whose density at N.T.P. is less than that of air. For example, in hydrogen the density is about 1/16 (actually 1/14·3) that of air, thereby giving a fourfold increase in velocity. Thus focussing would commence at frequencies four times those cited above.

As another instance we may take the case of water, where the velocity of propagation of pressure waves is approximately four times that in air. Here also the focussing would commence at frequencies four times those cited above.

The effect of focussing is to reduce the acoustic pressure on the disk, and, depending upon the mechanism driving the disk, the power radiated as sound is modified accordingly. For instance, with a coil-driven disk 10 cm. radius the power decreases to a very low value at high frequencies. In the upper audio-frequency register the amplitude of motion $X \propto 1/f^2$. If the amplitude varied so that $B\omega^2X^2$ (or $B\omega^2Y^2$) were constant, the power would be constant, but the axial pressure would increase with the frequency.

When G becomes oscillatory, the value is approximately unity, so that the pressure on the disk is $P_{r.m.s.}=2\rho_d Ac\omega Y$ and the power radiated $2\rho_d Ac\omega^2Y^2$. At the higher frequencies $Y \propto 1/f^2$, and it follows that the pressure falls off as $1/f$ and the power as $1/f^2$, provided, of course, the current in the coil is constant.

(5) *Accession to Inertia due to Motion of Disk.*

In addition to the acoustic pressure or useful work component, there is a second component of the total pressure on the disk. This component is in quadrature with the acoustic pressure, and can be regarded as an accession to inertia which is to be added to the mass of the disk*. According to Rayleigh, the accession to inertia—which is due to the

* 'Sound,' *loc. cit.* At frequencies where the wave propagation is sensibly plane the accession to inertia is evanescent.

waves diverging from the source—for both sides of the disk is given by the expression :

$$M_1 = \frac{\rho_d \pi K_1(2ka)}{k^3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

Putting $2ka = z$, we have

$$K_1(z) = \frac{2}{\pi}\left[\frac{z^3}{1^2 . 3} - \frac{z^5}{1^2 . 3^2 . 5} + \frac{z^7}{1^2 . 3^2 . 5^2 . 7}\right] - \text{etc.}, \quad (37)$$

or

$$\frac{\rho_d \pi K_1(z)}{k^3} = \frac{16a^3\rho_d}{3} = \frac{16a}{3\pi} \cdot \pi a^2 \rho_d, \quad . \quad . \quad . \quad (38)$$

which means that the inertia component is equivalent to a cylinder of air whose radius is that of the disk and whose height is $16a/3\pi$. The error involved in this assumption is about 5 per cent. when $ka = 0{\cdot}43$ and increases for higher values of ka. As ka increases, the value of M_1 decreases, *i. e.*, the accession to inertia is reduced. For a disk of given size the inertia effect falls off as the frequency rises above the value which satisfies the relation $ka = 0{\cdot}43$. Thus, for a disk 10 cm. radius at $50 \sim$ $M_1 = 7{\cdot}0$ gm., whereas at $1000 \sim$ it is only 2·4 gm. For a small disk say, 2 cm. radius, the value of M_1 is almost constant up to $1000 \sim$. Moreover, although the value of M_1 increases with the size of the disk, the frequency range—from zero upwards—over which it remains sensibly constant decreases. Thus, with a large diaphragm driven by an alternating force of *constant magnitude* the radiation in the bass register will be defective due to inertia effect.

The decay in inertia effect is due to interference, since the solid angle over which the radiation extends gradually diminishes, *i. e.*, the divergence decreases as the frequency increases. Furthermore, the energy distribution within the angular space is not uniform, but tapers away from the axis outwards.

The function $K_1(2ka)$ is plotted in fig. 4 partly from equation (37). Rayleigh gives an alternative series for this function, which is more amenable—and was therefore used—to the computation of $K_1(z)$ for large values of the argument than that of equation (37). It is of interest to mention that when z is very great $K_1(z)$ tends to the value $2z/\pi$, which is also very great.

(6) *Simple Formulæ for Air-pressure and Power radiated.*

From sections 4 and 5 we can deduce simple formulæ which are applicable under certain conditions at high and low frequencies.

At low frequencies, when $ka < 0{\cdot}4$ the value of G is

$$\frac{k^2a^2}{2} \quad \text{and} \quad M_1 = \frac{16}{3}a^3\rho_d,$$

which is constant. Thus

$$B = \rho_d A c k^2 a^2$$
$$= \frac{\rho_d A^2 \omega^2}{\pi c}, \quad \ldots\ldots \quad (39)$$

since $A = \pi a^2$.

Also r.m.s. force = mass × r.m.s. acceleration.

$$F = m\omega^2 X$$
$$= m\omega^2 Y,$$

where F, X, and Y are r.m.s. values for a sine-wave motion (phase not in question).

But the pressure on the disk

$$= B\omega Y$$
$$= \frac{\rho_d A^2}{\pi c}\left(\frac{F}{m}\right).\omega. \quad \ldots\ldots \quad (40)$$

Thus the pressure on the disk increases directly with the frequency.

Power radiated $= B\omega^2 Y^2$

$$= \frac{\rho_d A^2}{\pi c}.\frac{F}{m} = \text{a constant}. \quad \ldots\ldots \quad (41)$$

Moreover, the power radiated at low frequencies is constant, *provided* F *is constant*, *i. e.*, when the coil current is constant, in spite of the fact that the total pressure on the disk decreases in proportion to the frequency. This apparent paradox is explained when we realize that the amplitude of vibration increases inversely as the square of the frequency.

At high frequencies where $ka > 1{\cdot}9$ the wave propagation is sensibly plane and the value of G oscillates about unity. Taking its value as unity, *i. e.*, neglecting the oscillation of G, we have

$$B = 2\rho_d A c = \text{a constant}$$

and

$$B\omega Y = 2\rho_d A c.\frac{F}{m}.\frac{1}{\omega}, \quad \ldots\ldots \quad (42)$$

so that the pressure on the disk now varies *inversely* as the frequency (compare with equation (40)).

Power radiated $= B\omega^2 Y^2$

$$= 2\rho_2 A c \left(\frac{F}{m}\right)^2 \cdot \frac{1}{\omega^2} \cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

Thus the power radiated at high frequencies varies inversely as the square of the frequency, provided the coil current is constant.

(7) *Illustration of Analytical Expressions.*

The ultimate performance of the device under consideration depends, amongst other things, upon the current in the moving coil. To determine this, it is imperative to know

TABLE I.

Radius of disk = 5 cm. Mass of disk = 2·5 gm.

f. Frequency (cycles per second).	m. Effective mass (gm.).	$\cos\theta$. Acoustic power factor.	C_m. Motional capacity (microfarad).	R_m. Acoustic radiation resistance (ohms).	η. Efficiency per cent.
50	8·36	$2{\cdot}8\times10^{-3}$	0·33	26	0·52
100	8·36	5·7	0·33	26	0·52
200	8·36	11·4	0·33	26	0·52
500	8·3	28·5	0·33	26	0·5
1000	8·16	52	0·33	25	0·46
2000	7·82	69	0·31	17·5	0·3
4000	7·53	36	0·3	4·8	0·08
8000	7·5	18	0·3	1·2	0·018

m, $\cos\theta$, C_m, and R_m. These factors have been calculated for three disks of different sizes, namely, 5 cm., 10 cm., and 15 cm. radius respectively. Moreover, the influence of the size of the disk can be seen. The results have been tabulated and are given in Tables I., II., and III. The effective mass is the sum of that due to disk, coil (5 gm.) and accession to inertia.

The variation in effective mass is more pronounced the greater the diameter of the disk. In each case the mass decreases with rise in frequency, which can be attributed to reduction in the accession to inertia caused by the interference effect described in a former paper *. The acoustic

* McLachlan, Proc. Roy. Soc. A, vol. cxxii. p. 604 (1929).

power factor, and therefore the total sound-pressure on the disk, increases with the diameter *. In each of the three cases the power factor attains a maximum value. This is

TABLE II.

Radius of disk = 10 cm. Mass of disk = 10 gm.

f. Frequency (cycles per second).	m. Effective mass (gm.).	Cos θ. Acoustic power factor.	C_m. Motional capacity (microfarad).	R_m. Acoustic radiation resistance (ohms).	η. Efficiency per cent.
50	22	$1{\cdot}8\times10^{-2}$	0·88	66	1·3
100	22	3·6	0·88	66	1·3
200	22	7·2	0·88	66	1·3
500	20·2	17	0·81	69	1·3
1000	17·4	25	0·7	58	1·07
2000	15·2	14	0·61	18	0·31
4000	15	7	0·6	4·5	0·07
8000	15	3·5	0·6	1·1	0·015

TABLE III.

Radius of disk = 15 cm. Mass of disk = 22·5 gm.

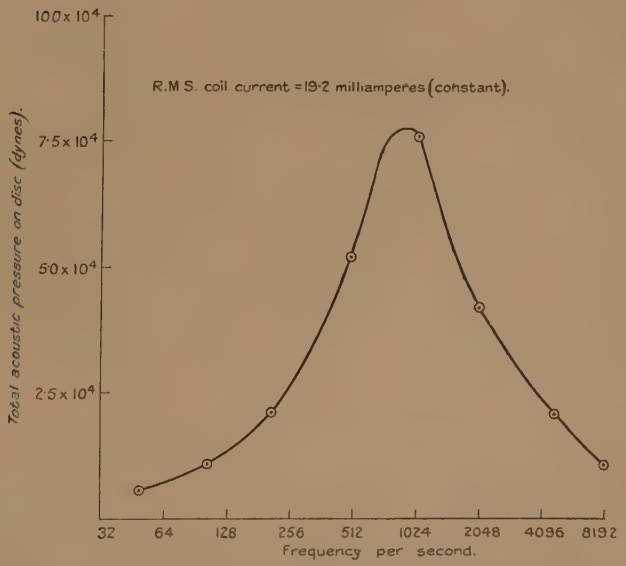
f. Frequency (cycles per second).	m. Effective mass (gm.)	Cos θ. Acoustic power factor.	C_m. Motional capacity (microfarad).	R_m. Acoustic radiation resistance (ohms).	η. Efficiency per cent.
50	50·7	$3{\cdot}77\times10^{-2}$	2·0	59	1·18
100	50·7	7·2	2·0	57	1·17
200	49·5	14·5	2·0	58	1·15
500	40·4	32	1·66	59	1·13
1000	29·3	35	1·14	46	0·85
2000	27·5	17·1	1·1	12	0·21
4000	27·5	8·7	1·1	1·3	0·02
8000	27·5	4·4	1·1	0·3	0·005

explained by a consideration of the velocity of the disk and the interference at various frequencies.

* The variation in the total pressure (inertia and acoustic components) has been treated by A. G. Warren, Proc. Phys. Soc.

Assuming the axial driving force and the effective mass to be constant, the power radiated is also constant. The acoustic pressure is power/velocity ; and since velocity $\propto 1/f$, the pressure increases with frequency, provided the wave propagation is spherical, *i. e.*, the waves are divergent about the source. But a point is reached when the propagation deviates from the spherical variety and gradually assumes the nature of plane waves. Moreover, as the frequency increases from 50 cycles upwards, a turning-point is reached due to interference, where the total pressure on the disk

Fig. 5.



Curve showing total acoustic pressure on 10-cm. disk at various frequencies.

decreases. A curve illustrating this effect is given in fig. 5, whilst the analytical aspect of the problem is obvious from expressions 39, 40, 42.

The motional capacity which exists by virtue of the back e.m.f. induced in the coil due to its motion in the magnetic field, increases with the mass (and radius) of the disk. This is explained by the reduced axial motion and therefore lower velocity of the larger disk, which generates a smaller back e.m.f. In each case the motional capacity decreases with

rise in frequency, owing to the reduction in the accession to inertia of the disk.

So long as the wave propagation is spherical, the acoustic radiation resistance R_m is substantially constant. When, however, interference commences, R_m decreases until at 8000 ~ it is a small fraction of its value at 50 ~. From the tabular values it is seen that over the range 50 to 2000 cycles the greatest output is obtained from a disk 10 cm. radius. Above 2000 cycles the output is greatest from the smallest disk, viz., 5 cm. radius. If the mass of a disk driven by a constant axial force varies as the square of the radius, the radiation over a given band of frequencies increases with decrease in the size of the disk. At the higher frequencies this must be clear, since the interference effect is less prominent with small disks than with large ones, whilst at low frequencies the accession to inertia is less. Now, this is not in keeping with the results just quoted. The apparent paradox can readily be explained if we consider the effect of the coil. Its mass is a much greater proportion of the total mass with a small than with a large diaphragm. Hence the acoustic power factor and the output of the small diaphragm are reduced accordingly. Moreover, in the present system there is a certain radius of disk for which the acoustic output over a definite frequency band is a maximum.

The combined efficiency of the arrangement is given by the ratio *

$$R_m/(R_m+R_0+\rho), \quad \text{where} \quad (R_m+R_0+\rho)$$

is the total A.C. resistance of the circuit of fig. 2, including the valve. Owing to the lack of "coupling" between the disk and the transmission medium (air), and to the large values of R_0 and ρ, the efficiency is very low. When disks of 2·5 cm. radius are used, the "coupling" can be increased very materially by using a suitable horn, and an overall efficiency (including valve) of from 7 to 10 times the cited figures is obtained. In practice, however, to secure ample output in the low frequency register, the length of the horn has to exceed 10 feet, which is not always convenient.

(8) *Current in the Moving Coil.*

The coil current at any frequency is controlled by the impedance of the coil in motion, together with ρ, the internal

* The inherent efficiency is $\frac{R_m}{R_m+R_0}$ and is several times that of the overall efficiency, since the latter is reduced considerably by the valve.

alternating current resistance of the valve. The latter has been allotted an average value of 4000 ohms. The motional-coil impedance depends upon four factors, namely: (1) the effective resistance at rest, (2) the acoustic radiation resistance, (3) the effective inductance at rest, (4) the motional capacity. Items (1) and (3) have been ascertained by bridge measurements, whilst (2) and (4) have been calculated from the formulæ developed herein.

TABLE IV.

Effective Inductance and Resistance of 1000-turn coil fixed in electromagnet.

f. Frequency (cycles per sec.).	L_0. Effective inductance coil at rest (henry).	R_0. Effective resistance coil at rest (ohms).
50	0·27	960
100	0·26	1000
200	0·24	1050
500	0·2	1170
1000	0·15	1360
2000	0·13	1760
4000	0·12	2250
8000	0·11	2750

Details of Coil and Magnetic Field.

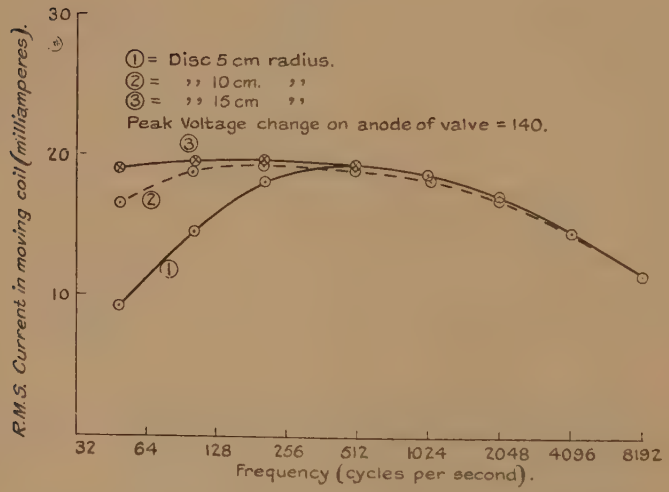
Mean radius of coil	$r=2{\cdot}5$ cm.
Number of turns of 46 enamelled wire.	$n=10^3$.
Mass of coil	$=5$ gm.
Mean strength of radial magnetic field.	$H=10^4$ c.g.s. units.
Coil constant	$C=\begin{cases} 2\pi rn\text{H}. \\ 1{\cdot}58\times10^8. \end{cases}$
Internal resistance of valve	$\rho=4\times10^3$ ohms.

The values of effective inductance and resistance of the coil when firmly fixed in the electromagnet with the field on are given in Table IV. Due to eddy currents in the iron the inductance decreases, whilst due to eddy current and hysteresis losses the resistance increases with rise in frequency. The former is useful, since it entails reduced inductive reactance and greater current at the upper frequencies. At these frequencies a movement of the order of 10^{-6} cm. produces quite an appreciable sound, and it is

difficult to fix the coil to prevent this occurring. However, as R_m is relatively small and C_m of negligible importance, any errors in measurement involved due to minute motion of the coil are immaterial. In fact, throughout the entire acoustic range, only a small error is involved if the inductance and resistance are determined with the magnet winding short-circuited upon itself, there being no radial field.

Using expression (13) and postulating a peak sine-wave voltage change of 140 volts on the anode of the valve, the coil current has been calculated for three disks at frequencies varying from 50 to 8000 cycles per second. The results

Fig. 6.



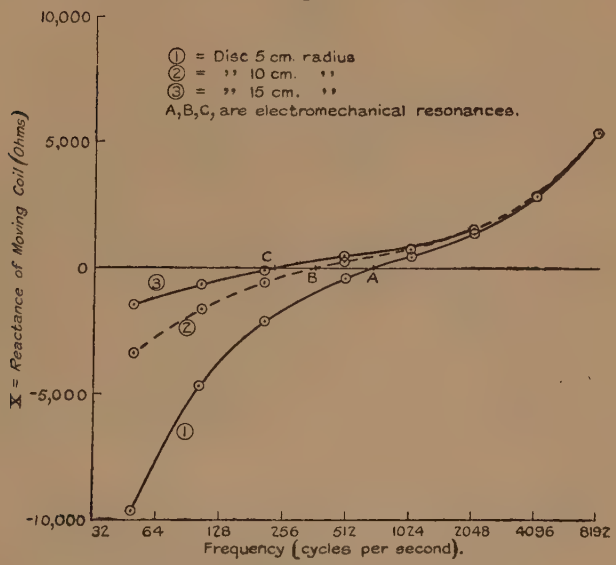
Curves showing current in moving coil at various frequencies.

are shown pictorially in fig. 6. At low frequencies the larger the diaphragm the larger the current. This is due to the lesser amplitude and velocity of the larger disk by virtue of its greater inertia. Thus the back e.m.f. induced by the motion of the coil in the magnetic field decreases as the radius of the disk increases. At the higher frequencies, although the induced e.m.f. is negligible, the coil current is curbed due to increase in the effective resistance (iron loss) and reactance of the coil. Moreover, the coil current at these frequencies is approximately the same for all three disks.

(9) *Reactance of Moving Coil.*

The reactance of the coil, namely $\left(w\mathrm{L}_0-\frac{1}{w\mathrm{C}_m}\right)$, varies from a negative value through zero to a positive value, the latter being due to its inductance. The negative reactance at low frequencies exists by virtue of the large back e.m.f. induced in the moving coil, *i. e.*, the motional capacity. Since the smaller the disk the larger the amplitude, and therefore the axial velocity, the low-frequency reactance of

Fig. 7.



Curves showing "reactance" of moving coil at various frequencies.

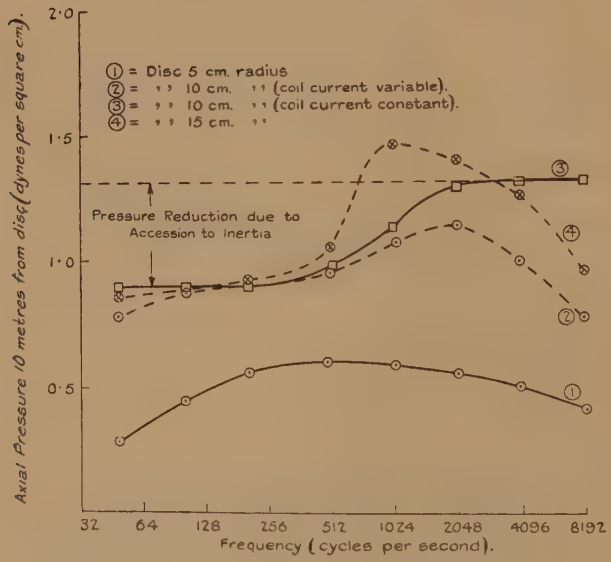
the 5-cm. disk is greater than that of the other two. When the reactance is zero, $w\mathrm{L}_0=\frac{1}{w\mathrm{C}_m}$, and this occurs at the electromechanical resonance frequency. The greater the effective mass of the disk and coil the lower the electromechanical resonance frequency. These points are depicted diagrammatically by the reactance curves of fig. 7. At frequencies above and below the resonance point, the current "lags" and "leads" respectively the impressed e.m.f. $\mathrm{E}=\mu\mathrm{E}_g$ of fig. 2. The further the frequency from

resonance the greater the "wattless" component of the current.

(10) *Axial Pressure.*

It has been shown * that the axial pressure at distances exceeding a certain number of diameters from the disk is independent of the frequency, so long as the acceleration of the disk is constant and f is not too high. This necessitates constant driving force and effective mass throughout the frequency range under consideration. In our particular

Fig. 8.



Curves showing axial pressure 10 metres from disk at various frequencies.

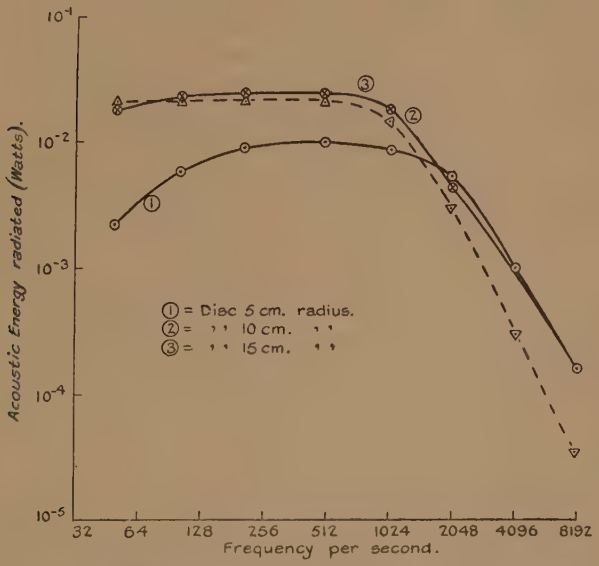
case both of these factors are variable. The deviation from constant pressure is seen from the curves of fig. 8. Curves 1, 2, and 4 indicate the pressure variation for the three disks when the current † and effective mass vary with the frequency. The pressure caused by the 5-cm. disk is relatively small, due to the influence of the mass of the coil, as explained previously. At the lower frequencies, there is little difference between

* Proc. Roy. Soc. *loc. cit.*
† See fig. 6.

the pressures caused by the 10-cm. and 15-cm. disks, but the pressure is greater for the 15-cm. disk at the higher frequencies, although the total energy output is less due to enhanced interference.

Curve (3) indicates the pressure variation for the 10 cm. disk when the driving force is constant. The smaller pressure at frequencies below 2000 cycles is due to the greater effective mass caused by "accession to inertia." In each case the oscillations in the curves at the higher frequencies concomitant with oscillation in the function G have been disregarded.

Fig. 9.



Curves illustrating power radiated at various frequencies.

(11) *Power radiated as Sound.*

The power radiated as sound from the three disks is portrayed graphically in fig. 9. The vertical scale is a logarithmic one, since the sensitivity of the ear progresses in a logarithmic manner. The output from the two larger disks is appreciably greater than that from the 5-cm. disk over the frequency range 50 to 1000 cycles. Thereafter the output from the larger disks falls off rapidly, until at the higher frequencies it is very small for all three disks.

This is, of course, due to interference concomitant with plane-wave propagation.

(12) *Transients.*

The preceding curves all relate to the steady state, and it remains, therefore, to indicate what results are to be expected when the e.m.f. applied to the grid of valve A_1 (fig. 1) is of a transient nature. The transformer is assumed not to affect the transient in any manner.

Taking the simplest case first, suppose the coil current is a replica in magnitude and time-displacement of the e.m.f. representing the transient as applied to the grid of the valve. Further, let us assume the disk to be so small that the accession to inertia is either constant or negligible over the important frequency range embodied by the transient. The force on the disk, and therefore its acceleration, is then a replica of the e.m.f. applied to the grid. But we have already shown * that the axial pressure at a point several diameters from the disk varies directly as the acceleration of the disk. Hence, under these conditions the acoustic reproduction of the transient at a point on the axis will be perfect, provided the pressure variations at the said point are in phase with the acceleration of the disk.

This is substantially correct when the frequency is small compared with the product of sound velocity and axial distance. If this condition is violated, there will be a phase-shift of the higher frequency components of the impulse, thereby altering its shape and causing distortion. Moreover, the higher the component frequencies of the transient the greater must be the distance from the disk to obtain distortionless reproduction.

With any of the three disks treated above, the effective mass varies with the frequency, and under a condition where grid e.m.f. and coil current were related linearly there would be a relatively reduced acceleration corresponding to the low-frequency components of the impulse. Thus the axial pressure of these components would be reduced relative to the high-frequency components, thereby causing distortion.

In the practical case, the coil current for a given e.m.f. applied to the valve grid depends upon the impedance of the complete anode circuit of the valve (see fig. 2 (a)). The current, as we see from fig. 6, varies appreciably with the frequency, there being a maximum value at the electro-mechanical resonance point. On either side of this frequency

* Proc. Roy. Soc. *loc. cit.*

the component sine-wave oscillations, into which the impulse can be analysed, are reduced in magnitude and altered in phase. Moreover, distortion occurs throughout the frequency range. By keeping the time-constant of the circuit as small as possible—3×10^{-5} is a practical figure,—the distortion of the components at the upper end of the frequency range can be reduced.

By combining the effect of variation in the effective mass of the disk with that due to variation in impedance, we obtain the resulting distortion of the transient. The effective mass of the disk and the driving force for a given e.m.f. both vary with frequency, so that the acceleration, and therefore the axial pressure, follow suit. The precise degree of distortion depends, of course, upon the shape of the transient, *i. e.*, upon the relative magnitudes and phases of its components.

Hitherto we have only dealt with the question of transients as registered by pressure variations on the *axis* of the disk. If we choose a point at an angular distance from the axis, we are faced with the evanescence of the higher frequencies due to interference. Moreover, to the preceding causes of distortion associated with transients the influence of focussing at the higher frequencies must be added.

It has been shown experimentally that in *the steady state* the ear is indifferent to the phases of the various component frequencies of a sound. From experimental observation the author is inclined to the view that this is inapplicable to transients. In the latter case it is probably the shape of the wave-front which counts, *e.g.*, gun-firing, piano, hand-clapping. The rapidity of response of the ear to sounds of varying suddenness has not been measured *, so that it is impossible to make any definite statement of the subject. It seems rational, however, that a degree of wave-front steepness is reached, after which the ear ceases to detect any difference in hearing sensation, *e.g.*, there is a saturation value †, although it may depend to an extent on the maximum pressure of the impulse. Also the possibility of supersonic sounds modifying the aural sensation of audible sounds must not be dismissed without experimental investigation.

Throughout this discussion of transients we have tacitly assumed that the coil is always in a constant radial field.

* So far as the author is aware.

† Above a certain value there is, of course, the sensation of pain.

A little consideration will show that with a transient consisting of a single pulse, the disk of fig. 1 will move out of the field and not return. Moreover, we postulate that for the purposes of the preceding discussion the coil always moves in a radial field whatever its position in space. In practice it is clear that the disk must be mounted on some form of elastic constraint at its periphery or elsewhere. In this case the equivalent electric circuit is indicated by fig. 3. When the coil is open-circuited, the disk has a natural frequency due to the elastic support; but when the circuit is closed, the resistance of the valve and coil are adequately low to provide large damping, thereby making the system quite aperiodic. It is easy to show that the critical resistance is

$$\frac{1}{2}\left[\frac{L'm}{C'm}\right]^{\frac{1}{2}}.$$

If the natural frequency is sufficiently low, say 3 per second, its effect on the frequency components above 50 cycles can be disregarded.

It is of interest to remark that in an actual moving coil loud speaker with a conical diaphragm, transients due to tympani cause a motion of the coil in one direction or the other which is visible to the eye.

We have made a tacit assumption, namely, that the instrument used for detection does not disturb the pressure distribution of the medium. At frequencies in the neighbourhood of 10,000 cycles the wave-length is so short (about 0·28 cm.) that the human body alters the pressure distribution very materially. The increase in pressure at the higher frequencies caused by diffraction due to the head can be calculated by assuming it to be spherical. Thus the distribution will vary from observer to observer. Moreover, when the variations in aural sensitivity and sensation are added, it is clear that a transient will not sound identical to all observers.

CXV. *A Study of the Three-Electrode Vacuum-Tube Oscillator.—Conditions for Maximum Current.* *By* E. T. Cho, *Ph.D., Indiana University, Bloomington, Indiana, U.S.A.**

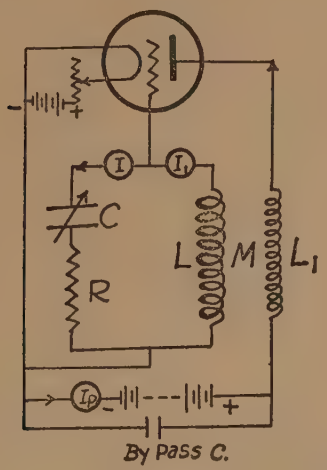
THE study is confined to one circuit, the "tuned grid" circuit. This circuit is shown in fig. 1, and consists of a three-electrode vacuum tube (201 A) in the grid circuit

* Communicated by Prof. R. R. Ramsey, Ph.D.

of which is connected the oscillating circuit, made up of a coil L and a variable condenser C.

In the plate circuit a "tickler" or feed-back coil L_1 is connected in series with a B battery and a D.C. voltmeter. A voltmeter is used as a milliammeter to measure the D.C. component of the plate current. A fixed condenser is placed so as to by-pass the A.C. component of the current around the milliammeter and the B battery. The radio-frequency current is measured by means of a high-frequency ammeter which is placed in series with the variable condenser C. The coils L are made of No. 18 D.C.C. magnet wire, and the coils L_1 are made of No. 34 D.C.C. magnet wire; they

Fig. 1.



"Tuned grid" circuit.

are wound on a basket weave form, the diameter of which is about 4 inches.

With a given coil L and a given plate potential and constant filament current the problem is to adjust the condenser C, the inductance of the tickler coil L_1, and the coupling between the coils L and L_1 so as to get the maximum radio-frequency current in the oscillating circuit CLR.

The method of procedure is as follows:—With a given coil L and a tickler coil L_1 the coupling of L and L_1 is fixed, and the capacity C is changed until the radio-frequency ammeter gives the largest reading. Then the coupling between the coils is changed, and the condenser is again changed until

the greatest current is obtained. This process is repeated until the coupling is found which gives the largest current. The method is illustrated by the data given in part (*a*) of Table I. The best coupling for coils L and L_1 is marked "max." in the table.

A second coil L_1 is then used as a tickler coil, and the procedure is repeated. A third, fourth, etc. coil is then used in the position L_1 until the best combination to be used with the coil L is found. The data given by part (*b*) of Table I. illustrate the method. The data recorded here correspond to the data marked "max." in part (*a*) of the same table. The data in part (*b*) marked "max. max." give the best values of coil L_1, mutual inductance M, coupling

Table I.

	L.	L_1.	M.	*k*.	I.	C.
(*a*)	3·6	200	14·5	·54	61	·001235
			10·0	·38	67 max.	·001200
			6·0	·22	53	·001140
			3·0	·11	10	·000750
(*b*)	3·6	200	10·0	·38	67	·001200
		100	8·0	·42	113	·001030
		60	8·5	·58	119 max. max.	·000710
		30	5·9	·55	111	·000565

coefficient *k*, and capacity C, to give the maximum-maximum current with the given coil L, with constant plate potential and filament potential.

Table II. gives the data for maximum-maximum conditions for sixteen coils, or sixteen values of L, and is a summation of about three thousand separate determinations.

Table II. gives the value for sixteen coils used in the position L. The coils have 2, 3, 4–17 turns of wire. The values of the inductance L, L_1, and M in the tables are expressed in microhenries; the resistance R is expressed in ohms; the current I is expressed in milliamperes; the capacity C is expressed in microfarads; *k* is the coupling coefficient; λ is the wave-length expressed in metres. The wave-length is calculated from the formula $\lambda = 1884\ \sqrt{LC}$. These values as calculated are somewhat lower than the actual value of the wave-length as measured with a wave-meter.

The inductances L and L_1 were measured by the wave-meter method by connecting the coil to a calibrated variable condenser and tuning the circuit when it was coupled loosely to an oscillator of known wave-length. The mutual inductances M were measured by clamping the coils L and L_1 so as to hold them rigidly in the same relative position, and then coupling them first in series and measuring the inductance and then connecting them in series opposition and measuring the inductance again. From these two results the mutual inductance M is calculated.

TABLE II.

$E_f = 5{\cdot}5$ volts. $E_p = 90$ volts.

L.	L_1.	R.	k.	M.	I.	C.	Wave-length.
2·4	40	—	·52	5·0	100	0·000375	56·5
3·6	60	—	·57	8·5	119	·000710	95·3
5·3	100	—	·67	15·5	125	·001315	157·0
7·4	140	4·6	·64	21·0	135	·001830	218·0
9·7	200	4·2	·43	29·0	138	·002235	277·0
12·6	250	5·0	·62	35·0	138	·002710	349·0
15·4	315	4·6	·60	42·0	136	·004055	471·0
19·7	450	4·6	·53	50·0	137	·004055	566·0
22·3	450	4·6	·70	70·0	146	·006235	702·0
26·4	620	4·5	·62	80·0	145	·007175	816·0
30·3	620	5·0	·73	100·0	142	·008600	960·0
34·9	800	5·0	·60	100·0	145	·009155	1065·0
39·1	990	4·8	·68	135·0	144	·010955	1230·0
44·0	1190	5·0	·63	145·0	144	·011905	1370·0
47·9	1390	5·0	·62	160·0	145	·012500	1460·0
54·5	1390	4·7	·69	109·0	144	·013580	1620·0
Average ...		4·74	·61				

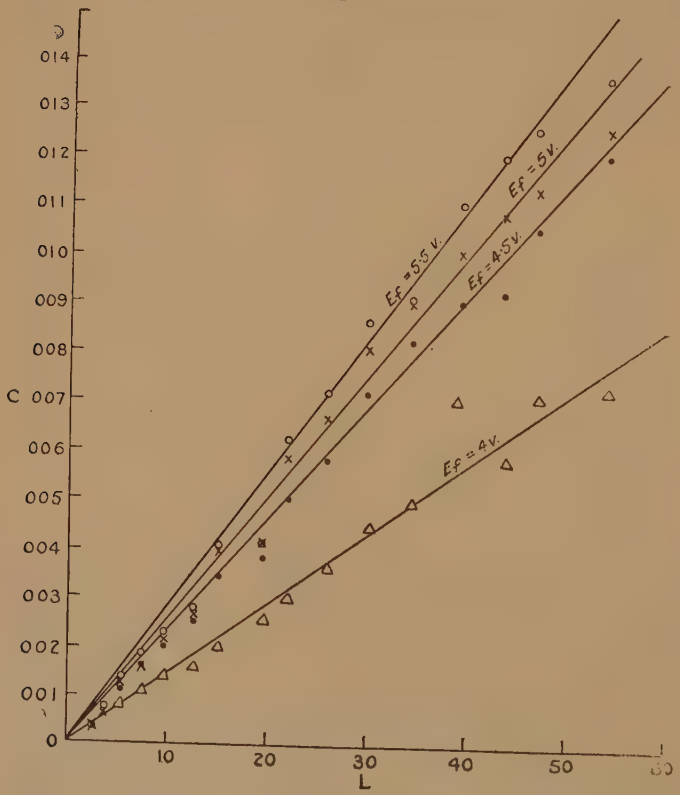
Table II. gives the conditions which give the maximum of maximum current for each of the sixteen coils when placed in the position L_1, when the filament potential E_f was 5·5 volts and the plate potential E_p was 90 volts. It will be noted that the resistance of the oscillating circuit as measured by the resistance variation method is about constant, the average value being 4·74 ohms. A large part of this resistance is due to the milliammeter. It will be noted that the frequency of the current through the small coils is much greater than the frequency of the current in the large coils.

The results have been collected in eleven other tables much like Table II. In these tables the filament potential E_f has

had the values 4, 4·5, 5·0, and 5·5 volts; the plate potential E_p had the values 88, 92, and 96 volts; the resistance of the circuit had the values 4·74, 5·74, 6·74, 7·74, and 8·74 ohms. The wave-length varied from 50 to over 1600 metres.

Since the tables are similar to Table II. they are not given here. The results of the twelve tables are shown in figs. 2, 3, and 4.

Fig. 2.



howing that L/C varies as $1/E_f^2$.

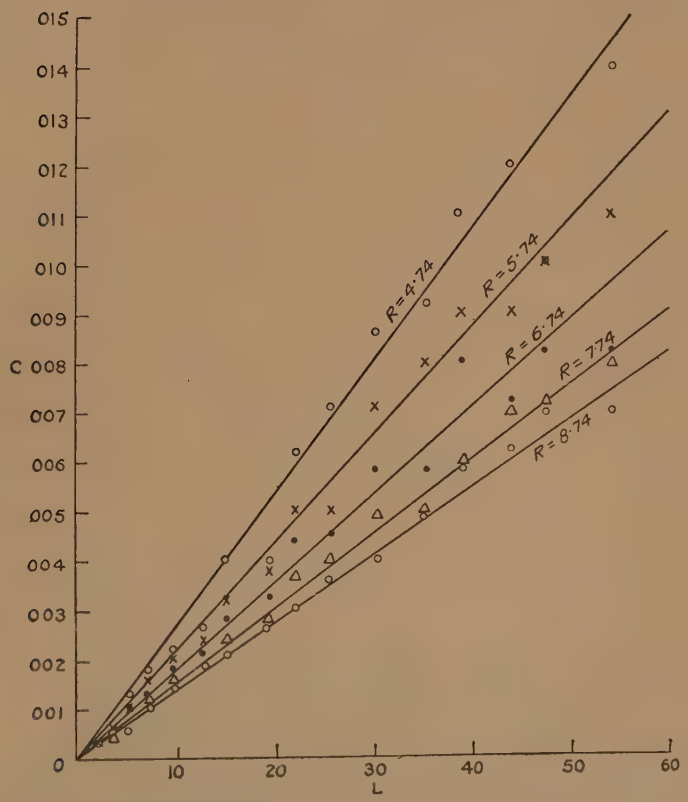
The curve marked $E_f = 5{\cdot}5$ volts is obtained by plotting the data for C and L in Table II. In these data the plate potential E_p was 90 volts and the resistance was about 4·7 ohms.

The three other curves are obtained from data like those in Table II. except that the filament potential has been changed to the values shown in the figure.

Figs. 2, 3, and 4 show the relation of L and C for various values: E_f's, R's, E_p's respectively.

In the figures the points do not fall exactly on straight lines, but the general direction of the points are straight lines. When one considers that the value of the tickler coil L_1 was necessarily changed by steps and the difficulties in getting exact values, the discrepancies can be laid to accidental errors.

Fig. 3.



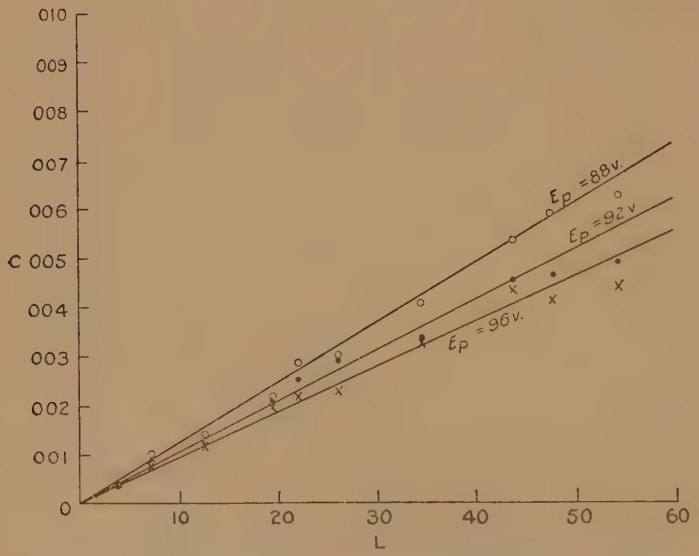
Showing that L/C varies as R.
These curves show the effect of added resistance. E_p=88 volts and E_f=5·5 volts. The ratio of C to L is constant.

These curves bring out the fact there is a simple relation of the inductance L to the capacity C of the tuned circuit when the constants of the oscillating circuit have been adjusted to give the largest possible current. This relation

depends upon the filament and plate potentials and the resistance of the circuit.

In fig. 5 the relation of M and L is shown. The data for this curve are taken when $E_f = 5{\cdot}5$ volts, $E_p = 90$ volts, and $R = 4{\cdot}74$ ohms, and a, amplification constant of the tube, equals 9. This shows that M/L is a constant, about 3·3, which is less than $a/2$; in this case $M/L = {\cdot}74\, a/2$. This suggests that perhaps $M/L = ka/2$, where k is the coupling coefficient.

Fig. 4.



Shows the effect of changing the plate potential of the tube. $R = 8{\cdot}7$ ohms; $E_f = 5$ volts.

Summing up the Experimental Results.

The ratio of L and C for "max. of max." current is some function of R, E_f, and E_p. We may conclude that

L/C varies as $1/E_f$	.....	Fig. 2
,, ,, R	.....	Fig. 3
,, ,, E_p	.....	Fig. 4

Therefore $L = h'' R E_p C / E_f$, where h' is a constant which for this 201 A tube has a value very near to 50 *.

* This value is calculated from the upper line of fig. 2.

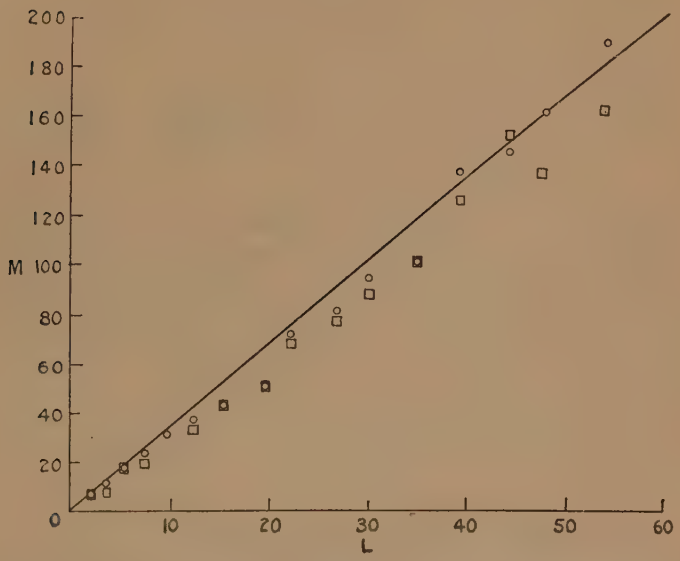
Then

$$L = hC, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (W)$$

where h is a constant depending upon the resistance R, the filament voltage E_f, and plate voltage E_p.

These data and equations can be used to determine the value of the inductances of the coils to give the max. max. current in any given case. As an illustration, suppose it is wished to construct an oscillator to give the maximum amount of current at 300 metres. Assume the resistances and potentials are such as to make the value of h equal 4830.

Fig. 5.



Showing that M/L=constant, which is less than theoretical value $a/2$. The ratio of M to L is nearly constant.

Two sets of data only are plotted. If all the data taken were plotted, the points would not fall farther from the straight line giving the mean value than the points given in the figure do.

The wave-length

$$\lambda = 1884 \sqrt{LC},$$

$$300 = 1884 \sqrt{LC} = 1884 \sqrt{hC^2} = 1884 \sqrt{4830}\, C.$$

Solving for C, we have C = 0·0025 mf.

Substituting this value in the equation $L = hC$, we have

$$L = 12{\cdot}1 \text{ mh.}$$

Since from fig. 5 $M/L = 3{\cdot}3$,

$$M = 40{\cdot}0 \text{ mh.}$$

Assuming the coupling coefficient is 0·7, from the relation $M = k\sqrt{LL_1}$,

$$L_1 = 265 \text{ mh.}$$

Theoretical Consideration.

Referring to fig. 1, we have the following equations :— For the plate circuit,

$$E_p = -M\frac{dI_1}{dt} - L_1\frac{dI_p}{dt}; \quad \ldots\ldots \quad (I)$$

for the grid circuit,

$$E_g = -L\frac{dI_1}{dt} - RI_1 - M\frac{dI_p}{dt}, \quad \ldots \quad (2)$$

$$R_pI_p = E_p + aE_g, \quad \ldots\ldots\ldots \quad (3)$$

where I_p is plate current, E_p is plate potential, I_1 and I are currents in the grid circuit assumed to be equal, E_g is the grid potential, L and L_1 are inductances, R is resistance, M is mutual inductance, a is the amplification constant of the tube, R_p is the plate resistance including the resistance of the voltmeter and coil L_1. By proper manipulation we get

$$\left(\frac{LL_1 - M^2}{R_p}\right)\frac{d^3I}{dt^3} + \left(L + \frac{L_1R}{R_p}\right)\frac{d^2I}{dt^2} + \left(R + \frac{L_1 + aM}{CR_p}\right)\frac{dI}{dt} + \frac{I}{C} = 0. \quad \ldots\ldots \quad (4)$$

By assuming that $I = I_0 \sin \omega t$, we have

$$\omega^2 = 1/LC \quad \ldots\ldots \quad (5)$$

and

$$-aL/2 - q < M < -aL/2 + q. \quad \ldots \quad (6)$$

Note.—Equations (4), (5), and (6) are derived in several places, one being Morecroft's 'Radio Communication,' p. 597, and need not be derived here.

In order to determine the possible condition of I from equations (1) and (2), multiply (1) by M and (2) by L_1 and subtract the results; we get

$$ME_p - L_1E_g = -M^2\frac{dI_1}{dt} + L_1L\frac{dI_1}{dt} + L_1I_1R,$$

but

$$I_1 = I.$$

Dropping the I_1 and merely writing I. and integrating

$$\frac{-t}{-M^2+LL_1}+h=\frac{\log\left(L_1RI+L_1E_g-ME_p\right)}{RL_1},$$

since $t=0$ and $I=0$, therefore the constant h becomes

$$\frac{\log(L_1E_g-ME_p)}{RL_1};$$

then the solution becomes

$$I=\left(\frac{L_1E_g-ME_p}{RL_1}\right)\left(e^{\frac{-L_1Rt}{LL_1-M^2}}-1\right). \quad . \quad . \quad (7)$$

From equation (7), when t becomes infinity, the current I becomes constant and equal to

$$I=ME_p/RL_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where E_g is negligible compared with other quantities. This equation shows the relation between I and M, E_p, L_1, R.

Substituting $k\sqrt{LL_1}$ for M, equation (8) becomes

$$I=\frac{E_pk\sqrt{L/L_1}}{R}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In equation (9), instead of having an independent variable expressed in terms of M, we have it expressed in terms of the coupling coefficient k.

This follows Ohm's law, since the current I is inversely proportional to the resistance. We may write the equation (8) in terms of a by substituting $Pa\,L/2$ for M.

$$I=PaLE_p/2RL_1, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where P is a constant.

From equations (9) and (10) I becomes

$$I=\frac{E_p(k\sqrt{L/L_1}+PaL/2L_1)}{2R}. \quad . \quad . \quad . \quad (11)$$

From equation (6) the mutual inductance M should be equal to about one-half of the inductance times the amplification constant of the tube for maximum current.

In fig. 5 the average value of $M/L=3{\cdot}3$, which is less than a divided by 2, since the amplification constant a equals about 9. This curve is plotted from data in which the current is maximum of maximum.

Again the third-order differential equation (4) can be reduced to a second-order equation if we assume that we have close coupling, or that $M^2=LL_1$ and that the value of

L_1R/R_p is very small compared with L. Making these substitutions, the equation becomes

$$L\frac{d^2I}{dt^2}+\left(R+\frac{L_1+aM}{CR_p}\right)\frac{dI}{dt}+\frac{I}{C}=0. \quad . \quad . \quad (12)$$

In order to solve equation (4) we have assumed that $k=$ unity. Table II. shows that, for maximum of maximum current, k has an approximate constant value of 0·61. Then L_1 is relatively small: the value of k approaches unity for maximum current, as is shown in Table III.

TABLE III.

L.	L_1.	M.	k.	I.
19·0	105·0	36·0	·78	58
		27·0	·60	57
		23·0	·51	53
		20·0	·45	53
		16·0	·36	46
		12·0	·27	38

We have shown that M/L is a constant in fig. 5, say b, and from theoretical assumption that $M^2=LL_1$. Then

$$L_1=b^2L.$$

Take equation (10) and express M and L_1 in terms of L. Then we get

$$L\frac{d^2I}{dt^2}+\left(R+\frac{b^2L+abL}{CR_p}\right)\frac{dI}{dt}+\frac{I}{C}=0$$

or

$$\frac{d^2I}{dt^2}+(R/L+u/C)\frac{dI}{dt}+\frac{I}{CL}=0, \quad . \quad . \quad (13)$$

where

$$u=\frac{b^2+ab}{R_p}.$$

The solution of (13) becomes

$$I=a_1e^{(k'+k'')t}+a_2e^{(k'-k'')t},$$

where

$$-\tfrac{1}{2}(R/L+u/C)=k'$$

and

$$+\tfrac{1}{2}\sqrt{(R/L+u/C)^2-4/LC}=k''.$$

When $t=0$, $I=0$. Then $a_1=-a_2$, and I becomes

$$I=A(e^{(k'+k'')t}-e^{(k'-k'')t}).$$

When the current is a maximum,

$$\frac{dI}{dt}=0$$

or

$$\frac{dI}{dt} = A[(k'+k'')e^{(k'+k'')t} - (k'-k'')e^{(k'-k'')t}] = 0.$$

Since t cannot be zero when the current is a maximum, the only way to make the equation equal to zero is to let k'' be zero.

Equating the value of k'', as given above to zero, expanding, and arranging in terms of powers of C/L and solving, we get C/L = a constant. This constant is expressed in terms of u and R, and is very approximately equal to $-u/R$.

Then

$$L/C = -R/u. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The negative sign is explained when it is remembered that M, the mutual inductance between the coils, is essentially negative.

The numerical value of R/u agrees with the value of h in the experimental equation $L = hC$.

Summary.

(*a*) In the case of the "tuned grid" circuit the equation has been solved, and the equation for the current is

$$I = E_p\left(\frac{k\sqrt{L/L_1}}{R}\right) = (aPL/2L_1)/R.$$

(*b*) In the case of the oscillating circuit made up of a primary coil whose inductance is L, a tickler coil L_1, and a variable condenser, it has been proved experimentally that when the circuit has been adjusted by changing both capacity and the mutual inductance between the coils until the maximum current has been obtained, then M/L = constant, which is somewhat less than the derived theoretical value. This holds true for circuit tuning from 50 to 1600 metres of wavelengths. This relation, as shown by equation (6), is

$$M = aPL/2 \quad \text{or} \quad M/L = aP/2 = \text{a constant.}$$

(*c*) The relation between L and C for maximum of maximum current is found by experiment, and is shown in the equations (W) and (14) to be

$$L/C = \text{constant.}$$

The value of the capacity C is much larger than that usually used in practice. These results apply for maximum current and not necessarily for maximum power or maximum efficiency.

CXVI. *The Transmission of Sound through Partitions. II.—Vibrating Partitions.* *By* A. H. Davis, *D.Sc., and* T. S. Littler, *M.Sc., Physics Department, The National Physical Laboratory, Teddington, Middlesex* *.

Abstract.

The paper is a continuation of previous work on the measurement of the transmission of sound through partitions of various materials. In the method the test panel covers an aperture in a sound-proof wall between two rooms. A beam of sound is directed obliquely upon one side of the partition, and upon the other side measurements are made of the sound transmitted. Whilst the earlier work was concerned largely with panels of a felt-like nature, the present paper gives results for partitions—ranging from a sheet of paper to single and double board partitions and to a brick wall—which transmit sound to a greater or lesser extent by vibration. It is found that, in spite of partition vibration, the sound is transmitted as a beam, and measurements of transmission ratio are largely independent of the position in the transmitted beam at which measurements are taken. To reduce errors associated with single-point observations, a moving microphone was found to be advantageous. As an additional aid in avoiding difficulties due to interference systems in the test room, a trial was made of the use of a note of fluctuating frequency.

The results of the measurements of sound transmission through panels of different types and weights are given, and a selection are exhibited graphically.

1. *Introduction.*

In a previous paper † the arrangements for measuring the transmission of sound by partitions of various materials were described. The test panel covered an aperture in a sound-proof wall between two rooms. On one side a beam of sound was directed obliquely upon the partition and, at points in the beam on the other side, measurements were made of the sound transmitted. Comparison with the transmission through the uncovered aperture gave the transmission ratio for the partition. The obliquity of the beam and the lagging upon the walls of the source

* Communicated by the Authors.

† Phil. Mag. iii. p. 177 (1927).

room prevented any reflexion of sound back to the source by the partition or walls, and obviated any acoustic reaction upon the source *. The lagging upon the walls, floor, and ceiling of the receiving chamber reduced the intensity of sound outside the main beam, and minimized stationary wave effects.

The earlier communication was chiefly concerned with panels of a felt-like nature, and the consideration of solid partitions and of the complications that might arise from their drum-like vibration was reserved until the present paper, which gives results for partitions of various types and weights—ranging from a sheet of paper to a brick wall—which transmit sound to a greater or lesser extent by vibration.

2. *Vibration of Solid Partitions.*

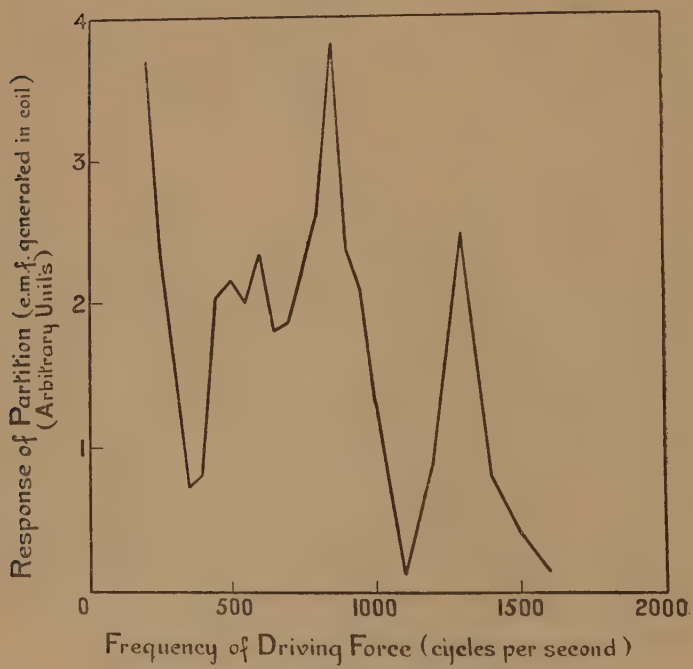
It appears from calculation that transmission through ordinary solid partitions is mainly due to flexural vibration of the panel, not to true acoustical refraction. With this in mind, some experiments were made on partition vibration. It was verified by simply touching the partition lightly with the fingers, that it was actually set in vibration by the sound. By applying an alternating mechanical force of constant magnitude to the central point, and observing the consequent velocity of vibration of the partition for a range of frequencies of the driving force, the curve of fig. 1 was obtained, showing the manner in which the response of a nominal $\frac{3}{8}$-inch fibre board varied with frequency for a mechanical driving force of constant magnitude. Various resonances within the acoustical range were revealed. Somewhat similar results were obtained for two other points of application of the driving force.

The driving of the partition and the measurement of the consequent amplitude of vibration were both carried out by making use of movements of loud-speakers of the type in which a coil of wire moves in the annular field of a pot-shaped magnet. For driving purposes the coil was attached to the partition and the magnet was separately supported. A known alternating current, $I \cos nt$, passed through the coil of length l_1, resulted in a mechanical force, $F = Il_1N_1 \cos nt$, being exerted upon the partition, where N_1 is the radial

* Owing to reaction upon the source when the incident beam was *normal* to the test partition, the apparent transmission through felt at 500 cycles per second was markedly increased (from 50 per cent. to 300 per cent.) by altering the distance of the source from the partition by one quarter of the wave-length of the sound.

magnetic flux-density at right angles to the wire of the coil in the annular gap of the electromagnet. To observe the consequent displacement, $A \cos(nt+\alpha)$, of the partition at any point, another coil was attached on the other side of the partition. The motion of this coil (of length l_2) moving in the field N_2 of its magnet, set up an e.m.f. (e) proportional to the velocity of the coil, and given by $e = N_2 l_2 A n \sin(nt+\alpha)$.

Fig. 1.



Response of partition under mechanical forcing.

Thus "e" was a measure of An, a quantity to which pressures and velocities in sound-waves are each proportional. By keeping the current I, and thus the driving force, constant whilst the frequency was varied, the determination of "e" gave a relative measure of the velocity of the partition at the point chosen.

The erection of the apparatus was quite simple. Two moving-coil receivers were taken and a piece of brass rod was screwed into the centre hole of each diaphragm, thus replacing the small bolt used for clamping the diaphragm to the frame upon which the coil is wound. Each rod was

securely attached so that the diaphragm, coil, and rod were rigidly connected. On the face of the partition a little hot sealing-wax was applied to points which were to be studied, in order to form a foundation for attaching the brass rods later. Each receiver movement was clamped to a rigid support, and its position adjusted until the end of the brass rod just touched the sealing-wax on the partition. The rod was then securely sealed to the partition by the application of a liberal amount of wax. When both movements were fastened in this way the diaphragm clamping screws were removed, and it was found that each coil moved freely with the partition. Under these circumstances very little constraint was exerted upon the partition by the measuring devices.

3. *Transmission of Sound through Solid Partitions.*

Following the experiments demonstrating partition vibration, measurements were then made of the transmission of sound through the above and other partitions in which vibration was expected to play a prominent part With felt-like partitions it had been found that the effect of covering the aperture had been to reduce the intensity of the transmitted sound in practically the same ratio at all points in the transmission room. This implied primarily that the oblique beam was transmitted unchanged in form. Since, however, the walls of the transmission chamber, although well lagged, were not completely absorbent, it implied also that the residual interference system set up in the chamber through partial reflexion to and fro by its boundaries was not markedly affected by substituting a felt panel for the area of open aperture which formed a portion of one side. It is unlikely that partitions with a hard non-absorbent surface are as satisfactory as felt in this latter respect.

In the present experiments with partitions likely to transmit sound by virtue of their mechanical (drum-like) vibration, it was necessary to ascertain whether the beam was transmitted unchanged in form or whether any appreciable amount of sound was sent out, say, in a direction perpendicular to the panel instead of in continuation of the oblique direction of the incident beam. Such an action would be inconvenient, as transmission ratios would depend upon the point in the room at which they were measured.

A somewhat analogous experiment with water-ripples directed obliquely upon a rubber membrane in a solid wall

between two halves of a ripple-tank had shown that beam transmission was possible when the fundamental frequency of the membrane was low *. Moreover, the size of the aperture (5 ft. × 4 ft.) in the acoustical tests of partitions was sufficiently great for the fundamental frequency of the building materials tested to be low compared with the frequency of the sounds concerned †.

In actual tests it was readily verified by ear for all types of partition tested that a pronounced beam was transmitted in the usual oblique direction, and that no undue amount of sound was sent out in other ways. Measurements by microphone further demonstrated that there was always a definite beam in the case of the transmitted sound, intensities at points off the beam being comparatively small.

For the fibre board which had been the subject of earlier tests on vibration, determinations of transmission ratio were made at a number of points off the main beam. As the intensities of sound at these points were relatively small, corresponding to from 3 per cent. to 40 per cent. of the maxima observed in the beam, the points were, of course, of secondary importance as regards the total energy transmitted by the partition. The average transmission ratio determined for a given frequency at points off the track of the beam did not, however, in general differ from that obtained in the main beam by more than 25 per cent. In one case, namely at a frequency of 800 cycles per second, the ratio off the beam was abnormally high, but even in this case a point on the perpendicular through the centre of the partition gave normal values, indicating no special concentration of sound in a direction perpendicular to the partition.

4. *Measurements by Point-to-Point Method.*

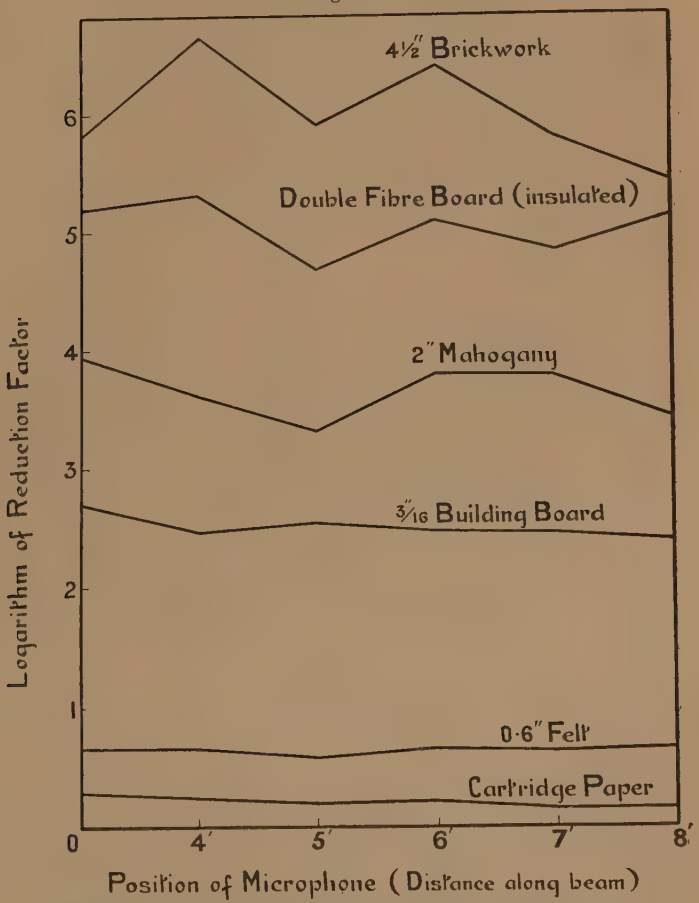
In the case of several other partitions, measurements of the transmission ratio were made at a number of points spaced 1 foot apart along the axis of the beam. Results for a frequency of 1000 cycles per second are given graphically in fig. 2 for various distances from the partition. Since the sensation of loudness in the human ear is closely related to the logarithm of the intensity of the exciting sound, a logarithmic scale of intensity is used. For convenience where logarithms are concerned, the reciprocal of

* Davis, Proc. Phys. Soc. 1926.

† This may well prove to be the criterion determining the minimum size upon which tests of practical value may be conducted with building materials.

the transmission ratio (known as the reduction factor) is employed instead of the transmission ratio itself. It will be seen that, whilst results for the heavier partitions are not so uniform as those for felt, the values for a given partition

Fig. 2.



Sound transmission through various partitions measured at a series of positions in the beam.
(Frequency of note—1000 cycles per second.)

show no systematic dependence upon the point at which measurements were taken.

On the whole, therefore, it was concluded that the beam was transmitted substantially unchanged in form, but that

to reduce errors from various causes it was desirable to take an average of the results obtained at a number of points.

5. *Averaging by Moving Microphone.*

To reduce the work involved in taking averages, experiments were made to test whether they could be obtained automatically by swinging the microphone to and fro along the sound beam in the test room, only the average e.m.f. set up in the cycle being measured.

A rigid suspension system attached to a point near the ceiling of the chamber was arranged for swinging the microphone in a definite manner in a vertical plane along the sound beam, the region thus explored being near to the standard positions at 4, 5, and 6 feet from the aperture. Owing to its harmonic swing, the microphone moves more rapidly through its equilibrium position than through points near the extreme of its excursions, and in consequence the average obtained gives greatest weight to the extreme positions. Accurate reproducibility of swing is thus desirable. Consequently a pointer and scale was erected to facilitate accurate observation of the amplitude of swing, which was maintained constant and of standard magnitude by impulses suitably applied.

Incidentally a second microphone was swung near the source in the other room. Owing to the obliquity of the beam of sound and the lagging upon the walls of the source chamber (see earlier paper) the reading of this microphone was practically the same whether a partition covered the test aperture or not. Consequently it serves in tests as a convenient check upon the constancy of the loud-speaker from day to day and week by week, a detail which is sometimes important.

For measuring the e.m.f. from the microphone an arrangement involving an amplifier and a detector was used. As detector, an instrument—such as a vacuo thermojunction—having sluggish action and square-law characteristics would be very suitable; for it would give minimum fluctuations of galvanometer deflexion and, in averaging the square of acoustical amplitude, would thus be averaging the sound-energy. Actually, in spite of its speedier response, a crystal detector was employed, on account of its greater sensitiveness and robustness; it had approximate square-law characteristics.

To compare the results obtained by a swinging microphone with those due to point-by-point calculation, measurements

of sound transmission were made by the two methods both for a compressed building board and for a $4\frac{1}{2}$-inch brick wall. In all cases the figures due to the swinging microphone lay within the limits of variation of individual measurements in the point-to-point exploration, of which some idea has been given in fig. 2. The actual results of the comparisons are included in Table I. later, where the two sets of results for each partition (Nos. 11 and 26) are given in juxtaposition. For the compressed board the differences are barely sufficient to be ordinarily detected by ear. For the brick wall wider variations occur, but the sound reduction is so much greater that the variations are not very serious from a practical point of view.

6. *Use of Sound Source of Variable Frequency.*

As an additional aid in avoiding difficulties due to the residual interference system which had survived the application of lagging to the walls of the receiving room, trial was made of the use of a test-note of variable pitch. This note was obtained from a loud-speaker operated by a valve oscillator, the tuning circuit of which contained a variable inductance driven by means of an electric motor. By this device the frequency of the note varied cyclically by $\pm$ 10 per cent. some 25 times per second.

The arrangements adopted greatly reduced the residual interference system in the transmitted beam, and were used in a few tests.

It appeared, however, that the moving microphone in the lagged room was generally satisfactory with a pure note of fixed frequency, and as there are some disadvantages in the use of the variable note in present circumstances, the fixed note was ordinarily used in the tests. It was noted, for instance, that, with the variable note, resonances in the loud-speaker and microphone gave undue prominence to certain sources in the frequency band, so that the e.m.f. from the microphone was often very different from that of the electrical current driving the loud-speaker and from that of the sound. There was, consequently, some uncertainty—although perhaps not serious—in the character of the test-note. Moreover, with a single pure note it is quite legitimate to employ sharply-tuned measuring apparatus and circuits—an important consideration where parasitic electrical effects from outside sources in the neighbourhood of the chambers have to be circumvented

7. *Results and Tables.*

Results obtained for the transmission of sound through a number of materials and structures are given in Table I., the figures tabulated being the logarithms of the reduction factors of the partitions tested. Table II. is useful for converting logarithms of reduction factors to transmission ratios, and *vice versa*.

As explained earlier, the logarithmic figure is convenient on account of the close relation the sensation of loudness bears to the logarithm of the intensity of the sound concerned. The "reduction factor" is defined as the reciprocal of the "transmission ratio," this latter being the ratio between the quantities of sound energy transmitted through the test partition and through the uncovered aperture when the partition is removed.

The logarithms of the reduction factors are given to the nearest 0·05. This corresponds to practically the smallest loudness-change detectable by ear, even when the change-over between the sounds to be compared is instantaneous, and no difficulties with interference systems or with extraneous noise are involved. In practice larger differences of 0·1 or 0·2 are of little importance; as will be seen from Table I. (No. 9), they correspond only to the slight difference in loudness that can be caused by covering an open doorway with a sheet of paper. It requires a partition for which the logarithm of the reduction factor is about 6 to reduce to inaudibility a sound having the loudness of an ordinary voice.

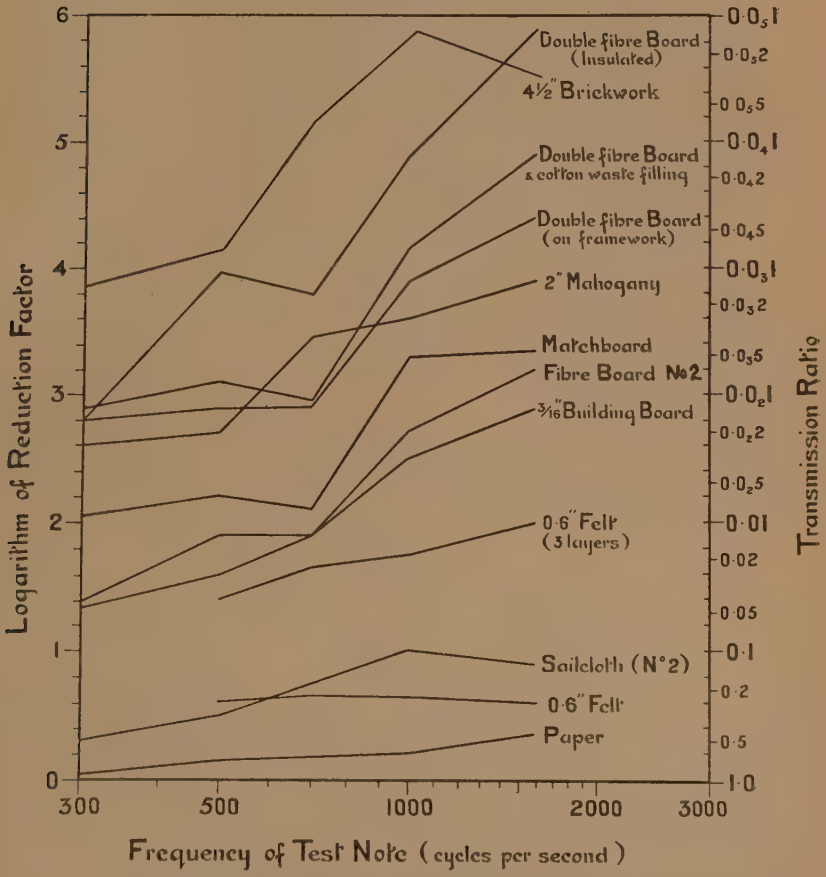
The partitions tested cover a wide range of transmission ratio, varying from a transmission of some 5–35 per cent. for cartridge paper to a few parts in a million for a brick wall. Fig. 3 presents graphically the results for a selected number of the partitions. A scale of ordinates has been included to the right of the graph so that transmission ratios may be read off if desired. In general, with the single non-porous partitions, the heaviest transmitted least sound.

Among the results may be noted figures for sailcloth of various types, this being a material sometimes used as a velarium for acoustic purposes in large halls. At 300 and 1600 cycles per second the light sailcloth transmitted respectively twice and six times as much sound as the heavy sailcloth.

Values for some simple compressed building boards are included. A certain fibre board was tested as a single board

clamped over the aperture, as a double partition with one layer of board on each side of a 4-inch wooden framework, as a double partition with the frame filled with absorbent (cotton waste), and as a double partition composed of two completely insulated boards. In the latter case one sheet of

Fig. 3.



Sound transmission through a variety of partitions for a series of notes of different frequencies.

fibre board was clamped over one face of the test-aperture, and another over the other face. As the two were thus, in fact, mounted upon the separate 9-inch brick walls which constitute the separation between the two test-rooms, they

were thoroughly insulated from each other. The air-space between them was 23 inches thick. In such a case the results show that each of the two insulated boards tends to have its full effect, the logarithm of the reduction factor for the two being of the order of the sum of the values for the separate boards. For some frequencies, however, the double partition falls short of this full effect, possibly through resonances of the intervening air, or even perhaps through differences of fixing in the erection of the boards. A layer of quilt hung in the interspace appeared to increase the insulation. Roughly speaking, the double-fibre board on a 4-inch frame gave results on the logarithmic scale lying half way between those for a single board and for two insulated boards. Filling the interspace with cotton waste slightly, but consistently, decreased the sound transmitted.

Figures for a 2-inch mahogany board, for a $\frac{3}{8}$-inch mahogany-faced plywood, and for matchboard fall intermediate between those for the single-fibre board and the double-fibre board on framework. One the whole, the single-brick wall is superior to the other constructions tested.

The authors desire to thank Dr. G. W. C. Kaye, Superintendent of the Physics Department, for continued interest and suggestions. Mr. W. J. B. Elliott, Junior Observer, again assisted with the experimental work.

TABLE I.

Sound Transmissions through Partitions.

No.	Description.	Partition. Thickness (in.).	Partition. Weight (lb. per sq. ft.).	Logarithm of Reduction Factor for Frequency (cycles per sec.). 300	500	700	1000	1600	Method of Test. Paragraph No.
	A. *Partitions clamped over aperture.*								
1.	Blanket.	—	—	—	—	0·20	—	—	4
2.	Felt (1 layer).	0·6	0·6	—	0·60	0·65	0·65	0·60	4
3.	Felt (2 layers).	1·2	1·2	—	1·05	1·15	1·15	1·20	4
4.	Felt (3 layers).	1·8	1·8	—	1·40	1·65	1·75	2·00	4
5.	Felt (4 layers).	2·4	2·4	—	1·85	2·05	2·30	2·65	4
6.	Sailcloth No. 1.	0·037	0·14	0·45	0·85	—	1·45	1·50	5
7.	Sailcloth No. 2.	0·025	0·09	0·30	0·50	—	1·0	0·90	5
8.	Sailcloth No. 3.	0·025	0·07	0·10	0·40	—	0·90	0·70	5
9.	Cartridge paper.	0·0088	0·031	0·05	0·15	—	0·20	0·35	4
10.	Eelgrass quilt.	0·5	0·20	—	—	0·50	—	—	4

TABLE I. (*cont.*).

No.	Partition. Description.	Thickness (in.).	Weight (lb. per sq. ft.).	Logarithm of Reduction Factor for Frequency (cycles per sec.). 300	500	700	1000	1600	Method of Test.
11.	Compressed board.	{ 0·19 0·19	0·61 0·61	1·35 1·40	1·60 1·60	1·90 2·0	2·50 2·55	2·90 2·85	4 5
12.	Mahogany-faced plywood.	0·6	1·4	2·10	2·40	3·30	3·30	3·80	4
13.	Mahogany.	1·85	4·9	2·60	2·70	3·45	3·60	3·90	4
14.	Fibre board No. 3.	0·29	0·46	1·05	1·65	1·65	2·45	3·10	4
15.	Fibre board No. 2.	0·46	0·66	1·40	1·90	1·90	2·70	3·20	4
16.	Fibre board No. 1.	0·50	0·75	1·55	1·90	1·95	2·90	3·40	4
17.	Fibre board No. 4.	0·42	0·57	—	1·65	2·0	2·60	2·60	6*
18.	Fibre boards Nos 3 and 4, with layer of eelgrass quilt sandwiched between.	--	—	1·10	2·55	2·45	—	2·75	5
19.	Double-fibre boards Nos. 2 and 4, insulated by an air-space 23 in. wide.	—	—	2·80	4·0	3·80	4·90	5·90	4
20.	Double fibre boards Nos. 3 and 4, insulated by an air-space 23 in. wide.	—	—	—	3·75	3·90	4·55	4·75	6*
21.	As 20, but with a layer of eelgrass quilt hung loosely in interspace.	—	—	—	3·85	5·45	5·95	5·45	6*
	Partitions on framework of 1½ in. *wood*, 62×46×4½ in. *in size, built into aperture.*								
22.	Double-fibre boards Nos. 2 and 4.	—	—	2·80	2·90	2·90	3·90	4·40	5
23.	As 22, but interspace filled with cotton waste (1·3 lb./sq. ft.).	—	—	2·90	3·10	2·95	4·15	4·90	5
24.	Matchboard. Each strip 46×5×½ in.	—	1·31	2·05	2·20	2·10	3·30	3·35	5
25.	Double matchboard. Each strip 46×5×½ in.	—	—	3·25	2·75	2·90	4·35	4·90	5
	Brick panels built into above wooden framework in aperture.								
26.	Fletton bricks and lime mortar.	{ 4½ 4½	41 41	3·85 3·75	4·15 4·00	5·15 5·35	5·90 5·90	5·50 5·10	5 4
27.	Fletton bricks and lime mortar (replaced in aperture; fine cracks visible).	4½	41	—	—	5·05	5·80	5·40	5

* For these experiments the frequency of the test-note varied cyclically over a frequency band ng within ±10 per cent. of the mean frequency.

Table II.

For use in conversions involving Transmission Ratios (t), Reduction Factors ($R=1/t$), and Logarithms of Reduction Factors ($\log_{10}R$).

The table gives the first two significant figures of the *transmission ratio* and of the *reduction factor* corresponding to given values of the *logarithm of the reduction factor.*

Mantissa of $\log_{10}R$.	Significant figures of	
	t.	R.
·00	10	10
·05	89	11
·10	79	13
·15	71	14
·20	63	16
·25	56	18
·30	50	20
·35	45	22
·40	40	25
·45	35	28
·50	32	32
·55	28	35
·60	25	40
·65	22	45
·70	20	50
·75	18	56
·80	16	63
·85	14	71
·90	13	79
·95	11	89

R=reduction factor. t=transmission ratio.

Examples:—

$\log_{10}R=0\cdot20$. $t=0\cdot63$. $R=1\cdot6$

$\log_{10}R=4\cdot20$. $t=0\cdot0_{4}63$. $R=1\cdot6\times10^{4}$.

$\log_{10}R=5\cdot20$. $t=0\cdot0_{5}63$. $R=1\cdot6\times10^{5}$.

Note the general relation between the characteristic of $\log_{10}R$ and the number of noughts after the decimal place in t. The only exception is when the logarithm is an exact integer; thus:

$\log_{10}R=5\cdot00$. $t=0\cdot0_{4}10$. $R=10^{5}$.

CXVII. *Critical Stresses for Tubular Struts.*

By H. Carrington, *D.Sc.* *

A SOLUTION of the problem of the stability of tubular struts with thin walls has been given by R. V. Southwell †, who deduced two formulæ giving the stresses at which instability occurs whilst the axis of the strut remains straight. One of these gives the stress which will cause a symmetrical distortion such that the lengths of diameter in any axial plane vary in a sinusoidal manner, the cross-section of the strut remaining circular. The other gives the stresses which correspond with lobed types of deformation, or those in which the lengths of diameters in both axial and cross-sectional planes vary in a sinusoidal manner. The latter formula has recently been stated to be incorrect by A. Robertson ‡, who maintained that the minimum collapsing stresses corresponding with the lobed types of deformation are either the same as, or higher than, that for the symmetrical type; whereas Southwell's formula for lobed types of deformation gives stresses which are less than that for the symmetrical type. It will here be demonstrated that Robertson's claim regarding the incorrectness of Southwell's formula is not justified.

It will first be shown briefly how the before-mentioned formulæ were deduced from Southwell's general equation. This is :

$$\psi^2\left[\frac{m+1}{2m}k^2q^4\right]+\psi\left[\frac{m-1}{2m}q^2\{(k^2+q^2)^2+k^2\}\right]$$
$$+\left(1-\frac{1}{m^2}\right)\frac{m-1}{2m}q^4+\frac{1}{3}\frac{t^2}{a^2}\psi q^2\left[\frac{m+1}{2m}k^2\{(k^2+q^2)^2-k^2\}\right.$$
$$\left.+\frac{m-7m+4}{2m^2}k^2q^2+\frac{m-1}{m}q^4\right]+\frac{1}{3}\frac{t^2}{a^2}\frac{m-1}{2m}\left[(k^2+q^2)^4\right.$$
$$-\frac{q^6}{m}-k^2(2k^4+7k^2q^2+\frac{7m^2+m-2}{m^2}q^4)$$
$$\left.+k^4+3k^2q^2+2\frac{m^2-1}{m^2}q^4\right]=0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $\psi=-\frac{m^2-1}{m^2}\frac{p}{E}$, p = stress, E = Young's modulus,

* Communicated by the Author.

† Phil. Trans. Roy. Soc. A, ccxiii. p. 187 (1913).

‡ Proc. Roy. Soc. A, cxxi. p. 558 (1928).

$\frac{1}{m}$ = Poisson's ratio, k = number of lobes, $q = \frac{2\pi a}{\lambda}$, λ = wave length of a lobe, a = mean radius of tube, and t = half-thickness of tube.

Taking first the terms which are independent of t^2, as was done by Southwell, and neglecting the square of $\psi -$, which must be small, we find

$$-\psi = \frac{m^2-1}{m^2} \frac{q^2}{(k^2+q^2)^2+k^2}. \quad . \quad . \quad . \quad . \quad (2)$$

If k is zero, it is easy to see that q must be great since ψ must be small. It will also be seen that if $k > 0$, the condition that ψ must be small is satisfied if q is small, but that this condition may also be satisfied if q is great. If $k=0$, equation (1) becomes

$$-\psi = \frac{1}{q^2} \frac{m^2-1}{m^2} + \frac{1}{3} \frac{t^2}{a^2} \left(2\psi + q^2 - \frac{1}{m} + \frac{2}{q^2} \frac{m^2-1}{m^2} \right). \quad (3)$$

Remembering that ψ must be small, it is easily found that the minimum value of p is

$$p = 2\mathrm{E} \frac{t}{a} \sqrt{\frac{1}{3} \frac{m^2}{m^2-1}}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

the corresponding value of q being given by

$$q^4 = 3 \frac{a^2}{t^2} \frac{m^2-1}{m^2}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In deducing the formula for the lobed type of distortion, Southwell considered only the case where q is small. If $k > 0$ and q is small, the important terms in equation (1) are

$$\psi q^2 k^2 (k^2+1) + \frac{m^2-1}{m^2} q^4 + \frac{1}{3} \frac{t^2}{a^2} k^4 (k^4 - 2k^2 + 1) = 0, \quad (6)$$

from which the minimum value of p is found to be

$$p = 2\mathrm{E} \frac{t}{a} \sqrt{\frac{1}{3} \frac{m^2}{m^2-1}} \left\{ \frac{k^2-1}{k^2+1} \right\}, \quad . \quad . \quad . \quad (7)$$

the corresponding value of q being given by

$$q^4 = \frac{m^2}{m^2-1} \frac{k^4 (k^2-1)^2}{3} \frac{t^2}{a^2}. \quad . \quad . \quad . \quad . \quad (8)$$

Formula (7) is Southwell's formula for lobed types of distortion. There is, however, the possibility that the case where q is great may yield smaller results than those given

by formula (7). Neglecting the unimportant terms in equation (1). when $k > 0$ and q is great, it becomes

$$\psi q^2(k^2+q^2)^2 + \frac{m^2-1}{m^2}q^4 + \frac{1}{3}\frac{t^2}{a^2}(k^2+q^2)^4 = 0. \quad . \quad (9)$$

The minimum value of this is

$$p = 2E\frac{t}{a}\sqrt{\frac{1}{3}\frac{m^2}{m^2-1}}. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The condition for this minimum is that q should have values given by

$$q = \frac{1}{2}\left\{\sqrt[4]{\frac{1}{A}} \pm \sqrt{\left(\frac{1}{A}\right)^{\frac{1}{2}} - 4k^2}\right\}. \quad . \quad . \quad (11)$$

If $k^2 > \frac{1}{4\sqrt{A}}$, the minimum value of p is greater than is given by (10).

Formula (10) is Robertson's formula for lobed types of distortion, and is exactly the same as Southwell's formula (4) for the symmetrical type.

It might here be noted that if $k=1$, Southwell's formula (6) reduces to Euler's formula for the buckling of a long tube where the axis does not remain straight after distortion of the tube. This case need not be considered further.

It is easily seen that Southwell's formula (7) gives smaller values for the critical stresses than Robertson's formula (10). For instance, if $m=2$ in (7) the value of p is only three-fifths of that given by (10). Formula (7) is therefore the more important.

In order to show conclusively that formula (7) is correct, it was decided to work out equation (1) in its entirety for two values of $\frac{t}{a}$. In Tables I. and II. $\frac{t}{a}=0{\cdot}001$ or $0{\cdot}02$ $m=\frac{10}{3}$, and $E=3\times10^7$ lb./in.^{2}. Four-figure logarithms were used throughout the calculations.

Columns A were calculated, using Southwell's formula (7) and the values of q from his formula (8). These values of q were then used in equation (1) and the results tabuated in column B. For the cases where $k=0$, formula (4), which is the same as Robertson's formula (10), and formula (5) were used instead of (7) and (8). The term containing ψ^2 in equation (1) was included in the calculation of the values

in column B, but its influence was found to be negligible. The lengths of half waves or values of $\frac{\lambda}{2}$ are also given in the tables for a tube 1 inch in mean diameter. The lengths for tubes of other diameters are, of course, directly proportional to these.

TABLE I.

k.	A. Tons/in.^{2}.	B. Tons/in.^{2}.	q.	$\frac{\lambda}{2}$ (in.) ($a=\frac{1}{2}$ in.).
0	16·21	16·21	40·65	0·07728
2	9·727	9·730	0·08521	36·86
3	12·97	12·99	0·2087	15·05
4	14·31	14·33	0·3812	8·242
5	14·96	14·99	0·6026	5·213
6	15·34	15·37	0·8733	3·597
8	15·71	15·81	1·563	2·011
10	15·89	16·03	2·447	1·283

$\frac{2t}{a}=0·002.$

TABLE II.

k.	A. Tons/in.^{2}.	B. Tons/in.^{2}.	q.	$\frac{\lambda}{2}$ (in.) ($a=\frac{1}{2}$ in.).
0	324·2	323·7	9·088	0·3456
2	194·5	198·9	0·3811	8·243
3	259·4	269·9	0·9335	3·365

$\frac{2t}{a}=0·04.$

It will be seen that agreement between the results in columns A and B is close. For the case $\frac{2t}{a}=0·002$, when $k=10$ the difference is less than 1 per cent., and for the case $\frac{2t}{a}=0·04$, when $k=3$ it is about 4 per cent. For the other cases given the differences are less than these.

In the light of the preceding investigation and the results given in Tables I. and II., it is inferred that Robertson's claim regarding the inaccuracy of Southwell's formula (7) is not justified. As a consequence of this claim, Robertson also mentioned that one of Southwell's diagrams (his fig. 6, p. 235) is incorrect. On comparing this diagram with the results given in Table II., it will be evident that this is not the case.

The problem has also been solved by J. Prescott * and W. R. Dean †, who deduced formulæ similar to numbers (4) and (7).

CXVIII. *On the Vacuum Bolometer as used in Measurements of Solar Radiation.* *By* N. Fairclough, *B.Sc.*‡

1. THE fundamental work on the Solar Constant carried out at the Astrophysical Observatory of the Smithsonian Institution is well known. Measurements of the solar radiation are made with the instrument known as the vacuum bolometer, and it is the object of the present paper to investigate a problem arising in the theory of the instrument §. The bolometer consists essentially of a delicate electrical thermometer, the sensitive parts being two fine tapes of metal, blackened on the front surface. One tape can be exposed to the sun's rays to be measured, while the other tape is screened from those rays. The tapes are joined by suitable resistance coils, and the whole made up into a Wheatstone's bridge. A small change in temperature in the exposed strip changes the resistance of that strip, and produces a deflexion of the sensitive galvanometer in the circuit. Prof. S. Chapman, F.R.S., suggested to the writer the desirability of investigating what is the best thickness of tape to be used in the instrument, and the following simple argument shows that there will in fact be an optimum thickness which makes the instrument most sensitive.

The tapes of fixed length and width, any temperature change in the exposed tape, due to a fixed amount of radiation, will depend upon the thickness of the tape. If extremely thin tapes are considered they will have very high resistances, and but very small currents will pass through each tape. On

* 'Applied Elasticity,' p. 530 (1924).
† Proc. Roy. Soc. A, cvii, p. 734 (1925).
‡ Communicated by Prof. E. A. Milne, F.R.S.
§ Annals of the Astrophysical Observatory of the Smithsonian Institution, iv. p. 45.

exposure, when the balance in the bridge is destroyed, the current passing through the galvanometer, and so the galvanometer deflexion, will be negligible. The current required for extremely thick tapes will be very large, but the tapes will have very low resistances, and, on exposure, the change in resistance will be small. The fraction of current through the galvanometer will be minute, and again we may expect a negligible deflexion. It may be inferred that between these extremes there is a thickness of tape that will give a maximum galvanometer deflexion.

2. *Nature of the Problem.*

Experimental work at the Astrophysical Observatory of the Smithsonian Institution has defined the best length and width of tape to use, namely, 1·6 cm. and 0·01 cm. respectively *. Accordingly, on this assumption, it will be the object of this paper to investigate what thickness of tape will render the bolometric apparatus most sensitive to solar radiation. The calculations will be applied to platinum tapes of rectangular cross-section. A few calculations of a similar kind have already been given by the Smithsonian observers (*loc. cit.*), but the present investigation is more complete.

The measure of the sensitiveness of the bolometer will be the magnitude of the galvanometer deflexion when the tape is exposed. Any deflexion, z, will depend upon C_g, the current passing through the galvanometer, and the resistance, g, of the instrument. If r_1 = resistance of tape to be exposed, r_3 = resistance of concealed tape, r_2, r_4 the resistances of the balancing coils ; then

$$C_g = f(r_1).$$

Also, there is one particular value of g for which the galvanometer deflexion is a maximum, subject to the remaining resistances in the bridge being constant. Thus, if n = thickness of tape, we require for an optimum thickness

$$\frac{d}{dn}\left[\left(\frac{dz}{dr_1}\right)_{r_1=\frac{r_2}{r_4}.r_3}\right] = 0, \quad . \quad . \quad . \quad . \quad (1)$$

subject to the condition

$$\frac{d}{dg}\left[\left(\frac{dz}{dr_1}\right)_{r_1=\frac{r_2}{r_4}.r_3}\right] = 0, \quad . \quad . \quad . \quad . \quad (2)$$

which fixes the value of g.

* Annals of the Astrophysical Observatory of the Smithsonian Institution, iv. p. 46.

3. *Steady State of Temperature along the Tape.*

(a) *No external radiation.*

Let θ = temperature of the bolometer tape in absolute degrees at a distance x from the centre. Let $2l, m$ be the length and width of the tape respectively, k the thermal conductivity, and γ the specific electrical conductivity of the material of the tape. Let σ = Stefan's constant of radiation, i = the electric current flowing through the tape in the steady state, and θ_1 = the absolute temperature at $x = l$. We assume this to be the temperature of the surroundings.

For tapes *in vacuo*, perfectly black on that face which receives the solar radiation, and perfectly reflecting on all others, there are three factors which combine to determine the temperature across any section. Consider a section of the tape of length δx, at the point x. The exchange of heat consists of

(i.) gain by conduction: this amounts to $kmn\frac{d^2\theta}{dx^2}.\delta x$;

(ii.) gain by generation of heat by the current: this amounts to $(0{\cdot}24\, i^2/\gamma mn)\delta x$, where i is measured in practical units;

(iii.) loss by radiation: this amounts to $\sigma(\theta^4 - \theta_1{}^4)m.\delta x$, where σ is measured in calories per cm.^{2} per second.

In the steady state the gain and the loss must balance, and we have the equation

$$kmn\frac{d^2\theta}{dx^2} + \frac{0{\cdot}24\, i^2}{\gamma mn} - \sigma(\theta^4 - \theta_1{}^4)m = 0 \quad . \quad . \quad (3)$$

or

$$\frac{d^2\theta}{dx^2} - A\theta^4 + B = 0, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where

$$A = \frac{\sigma}{kn} \quad \text{and} \quad B = \frac{0{\cdot}24\, i^2}{k\gamma m^2 n^2} + \frac{\sigma\theta_1{}^4}{kn}.$$

In any particular case A is constant, but B depends on γ, which itself depends on θ. To facilitate the integration of equation (4), we shall treat B, and therefore γ, as constant, and the value chosen will be the value of γ at the mean temperature over the tape. In a later part of the paper we shall investigate to what extent this assumption is in error.

If θ_0=the absolute temperature at the middle of the tape equation (4), on integration, becomes

$$\frac{1}{2}\left(\frac{d\theta}{dx}\right)^2 - \tfrac{1}{5}A\theta^5 + B\theta = -\tfrac{1}{5}A\theta_0^5 + B\theta_0,$$

since

$$\frac{d\theta}{dx} = 0 \quad \text{and} \quad \theta = \theta_0 \quad \text{at} \quad x = 0.$$

Therefore

$$\frac{d\theta}{dx} = -[2B(\theta_0 - \theta) - \tfrac{2}{5}A(\theta_0^5 - \theta^5)]^{\frac{1}{2}}$$

or

$$x = \int_{\theta}^{\theta_0} \frac{d\theta}{[2B(\theta_0 - \theta) - \tfrac{2}{5}A(\theta_0^5 - \theta^5)]^{\frac{1}{2}}} \quad . \quad . \quad . \quad (5)$$

The boundary condition is $\theta = \theta_1$, the external temperature at $x = l$, so that

$$l = \int_{\theta_1}^{\theta_0} \frac{d\theta}{[2B(\theta_0 - \theta) - \tfrac{2}{5}A(\theta_0^5 - \theta^5)]^{\frac{1}{2}}} \quad . \quad . \quad . \quad (6)$$

This equation determines the value of B for chosen temperatures θ_0, θ_1, and equation (5) will give the value of θ at any point x on the tape.

(b) *When external radiation of amount* R *per unit area falls on the tape.*

The resistance of the tape will now be increased. Let γ' be the new value of γ, and let i' be the new current. If θ' be the new temperature at the point x, we have, for the steady state of temperature along the tape, the equation

$$kmn\frac{d^2\theta'}{dx^2} + \frac{0{\cdot}24\, i'^2}{\gamma' mn} - \sigma(\theta'^4 - \theta_1^4)m + Rm = 0 \quad . \quad (7)$$

or

$$\frac{d^2\theta'}{dx^2} - A\theta'^4 + B' = 0, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where A is as before, and

$$B' = \frac{0{\cdot}24\, i'^2}{k\gamma' m^2 n^2} + \frac{\sigma\theta_1^4}{kn} + \frac{R}{kn};$$

so that

$$x = \int_{\theta'}^{\theta_0'} \frac{d\theta'}{[2B'(\theta_0' - \theta') - \tfrac{2}{5}A(\theta_0'^5 - \theta'^5)]^{\frac{1}{2}}} \quad . \quad . \quad (9)$$

if θ_0'=the new central temperature.

Considering the whole length of tape with the appropriate boundary condition,

$$l=\int_{\theta_1}^{\theta_0'}\frac{d\theta'}{[2B'(\theta_0'-\theta')-\frac{2}{5}A(\theta_0'^5-\theta'^5)]^{\frac{1}{2}}}. \quad . \quad (10)$$

This equation determines the value of B′ for chosen temperatures θ_0', θ_1, when equation (9) will give the new temperature θ' at the point x.

In equation (6) put $\theta=\theta_0.t$. Then, writing $\theta_1=\theta_0.\alpha$,

$$l=\int_{\alpha}^{1}\frac{(\theta_0)^{\frac{1}{2}}.dt}{[2B(1-t)-\frac{2}{5}A\theta_0^4(1-t^5)]^{\frac{1}{2}}}$$

$$=\int_{\alpha}^{1}\frac{(\theta_1)^{\frac{1}{2}}.dt}{[\alpha]^{\frac{1}{2}}[2B(1-t)-\frac{2}{5}A\frac{\theta_1^4}{\alpha^4}(1-t^5)]^{\frac{1}{2}}}.$$

As B increases for a fixed α, this integral decreases. Since it is constant and equal to l, as B increases α must decrease; that is, $\theta_0'>\theta_0$.

4. *Transformation of Equations for the Steady State.*

We have seen that external radiation falling on the tape will produce a rise in temperature at any point. There will be a mean rise in temperature, $\overline{\delta\theta}$, and on this the calculations of galvanometer deflexions for varying thicknesses of tape will be based. To obtain equations (5), (6), (9), (10) in forms more suitable for computation, we have, from equation (5),

$$x=\int_{\theta}^{\theta_0}\frac{d\theta}{\left[\frac{2A}{5}(\theta_0-\theta)\left(\frac{5B}{A}-\frac{\theta_0^5-\theta^5}{\theta_0-\theta}\right)\right]^{\frac{1}{2}}}$$

or

$$qx=\int_{\theta}^{\theta_0}\frac{d\theta}{\left[(\theta_0-\theta)\left(\lambda-\frac{\theta_0^5-\theta^5}{\theta_0-\theta}\right)\right]^{\frac{1}{2}}}$$

if

$$q=\left(\frac{2A}{5}\right)^{\frac{1}{2}}=\left(\frac{2\sigma}{5kn}\right)^{\frac{1}{2}} \quad \text{and} \quad \lambda=\frac{5B}{A}=5\left(\frac{0{\cdot}24\,i^2}{\gamma_M m^2 n\sigma}+\theta_1^4\right), \quad . \quad . \quad . \quad (11)$$

where γ_M is used to denote the value of γ at the mean temperature over the tape. Putting $\theta_0-\theta=y^2$,

$$qx=\int_0^{(\theta_0-\theta)^{\frac{1}{2}}}\frac{2dy}{[\lambda-(\theta_0^5-\theta^5)/(\theta_0-\theta)]^{\frac{1}{2}}}. \quad . \quad . \quad (12)$$

From equation (6),

$$ql = \int_0^{(\theta_0-\theta_1)^{\frac{1}{5}}} \frac{2dy}{[\lambda-(\theta_0^5-\theta^5)/(\theta_0-\theta)]^{\frac{1}{2}}} \quad . \quad . \quad . \quad (13)$$

Similarly, from equations (9) and (10), on changing the variable from θ' to θ,

$$qx = \int_0^{(\theta_0'-\theta)^{\frac{1}{5}}} \frac{2dy}{[\lambda'-(\theta_0'^5-\theta^5)/(\theta_0'-\theta)]^{\frac{1}{2}}} \quad . \quad (14)$$

and

$$ql = \int_0^{(\theta_0'-\theta_1)^{\frac{1}{5}}} \frac{2dy}{[\lambda'-(\theta_0'^5-\theta^5)/(\theta_0'-\theta)]^{\frac{1}{2}}}, \quad . \quad (15)$$

where

$$\lambda' = 5\left(\frac{0{\cdot}24\, i'^2}{\gamma_M' m^2 n\sigma} + \theta_1^4 + \frac{R}{\sigma}\right). \quad . \quad . \quad . \quad . \quad . \quad (16)$$

5. *General Method of Determination of Mean* $\delta\theta$.

We have in equations (12) and (13)

$$x = f(\lambda, \theta, \theta_0)$$

and

$$l = f(\lambda, \theta_1, \theta_0),$$

so that

$$\lambda = f(\theta_1, l, \theta_0)$$

and is determinate for tapes of fixed length when we have chosen the temperatures at the middle and ends.
Also,

$$\theta_0 = \phi(l, \lambda, \theta_1).$$

Therefore

$$x = f(\phi, \lambda, \theta)$$

and

$$\theta = F(x, l, \lambda). \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

Since λ is determinate, the temperature at any point x can be found.

When external radiation changes the central temperature to θ_0', the corresponding change in λ is to λ', and

$$\theta_0' = \psi(l, \lambda', \theta_1),$$

while

$$\lambda' = f(\theta_1, l, \theta_0').$$

Since θ_0' is arbitrary, λ' is determinate.

Differentiating equation (17),

$$\delta\theta = \frac{\partial F}{\partial \lambda} . \delta\lambda,$$

so that

$$\overline{\delta\theta} = \frac{\delta\lambda}{l} \int_0^l \frac{\partial F(x, l, \lambda)}{\partial \lambda} . dx$$

or

$$\delta\theta = \frac{\delta\lambda}{l} \psi(\lambda, l), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and is thus a quantity which can be found from the equations of the steady state.

6. *Electrical Resistance Calculation.*

To connect $\overline{\delta\theta}$ with the thickness of tape, we consider the change in resistance on exposure.

Let r_1' = resistance of the tape after exposure. The resistance dr_1, of a strip dx, before exposure, is

$$\frac{1}{\gamma} \cdot \frac{dx}{mn},$$

where

$$\gamma_1 = \gamma[1 + \alpha(\theta - \theta_1)]$$

and

γ_1 = the value of γ for $\theta = \theta_1$.

Thus,

$$dr_1 = \frac{1 + \alpha(\theta - \theta_1)}{\gamma_1 mn} . dx$$

and

$$r_1 = 2 \int_0^l \frac{1 + \alpha(\theta - \theta_1)}{\gamma_1 mn} . dx. \quad . \quad . \quad . \quad (19)$$

Then

$$r_1' = \int_0^l \frac{1 + \alpha(\theta' - \theta_1)}{\gamma_1 mn} . dx. \quad . \quad . \quad . \quad (20)$$

Therefore

$$\delta r_1 = 2 \int_0^l \frac{\alpha . \delta\theta}{\gamma_1 mn} . dx$$

$$= (2\alpha / \gamma_1 mn) . \overline{\delta\theta}, \quad . \quad . \quad . \quad . \quad . \quad (21)$$

which gives the mean rise in temperature in terms of the increment in resistance, and the thickness of the tape.

7. *Measure of the Galvanometer Deflexion.*

The best galvanometer resistance g, satisfying the fundamental equation (2), is given by the well-known formula

$$\frac{1}{g} = \frac{1}{r_1 + r_3} + \frac{1}{r_2 + r_4} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Also we have assumed (paragraph 2) that

$$C_g = f(r_1),$$

which $=0$, in the balance.

Thus

$$\delta C_g = f'(r_1) . \delta r_1$$

$$= (2\alpha/\gamma_1 mn) . \overline{\delta\theta} . f'(r_1)$$

by equation (21).

Using the value of g (constant) determined by equation (22), and differentiating

$$z = \kappa . g^{\frac{1}{2}} . C_g,$$

then

$$\delta z = \kappa . g^{\frac{1}{2}} . (\delta C_g)$$

or

$$\delta z = \kappa . g^{\frac{1}{2}} . (2\alpha/\gamma_1 mn) . \overline{\delta\theta} . f'(r_1) . \quad . \quad . \quad . \quad (23)$$

Equation (23) gives us a measure of the galvanometer deflexion on exposure to radiation. In assuming $C_g = f(r_1)$, we neglect the increment of current through the concealed tape when the resistance r_1 changes to r_1'. Whether or not this assumption can be justified will be more apparent when the method is applied to particular thicknesses of tape.

8. *Balancing Coils.*

We have placed no restrictions upon the relative magnitudes of the resistances in the bridge. In order that the two tapes may be under conditions as similar as possible, it will be assumed that they have equal dimensions, and so equal resistances, before exposure. Then the balancing coils, r_2, r_4, will have equal resistances, and equal currents, i, $(=\frac{1}{2}C)$ will flow through each tape. Also, by this choice, no current will flow through the galvanometer before exposure, and in consequence δz will in all cases be measured from the same zero.

9. *Application of General Method.*

By means of equation (23) we are attempting to measure the galvanometer deflexion δz, when a tape of known dimensions is exposed to radiant energy. The integration of equations (3) and (7) has for its object the determination of $\overline{\delta\theta}$ over the length of the tape, and by means of the integrals given in equations (12) to (15) this factor can be found. For, if in equations (12) and (13) we write L for

$$2\left[\lambda-\frac{\theta_0{}^5-\theta^5}{\theta_0-\theta}\right]^{-\frac{1}{2}},$$

and choose any particular value for λ, say λ_p, then for any value of θ, between θ_1 and θ_0, L is determinate. The area under the curve obtained by plotting corresponding values of θ and L will, by equation (13), be equal to ql or $(2\sigma/5kn)^{\frac{1}{2}}.l$, and for a given l, this will fix the value of n, corresponding to the value λ_p, to satisfy equation (13).

If, in addition, we find the ordinate up to which the area under the curve is equal to qx, $(x<l)$, we have determined the upper limit in the integral of equation (12). This gives the value of θ at the point x. Taking a series of values of x and θ, we shall know the temperature distribution over the tape of known thickness, when the temperature at the ends is θ_1 and the central temperature θ_0.

10. When the radiant energy of amount R per unit area falls on the tape we require to solve equations (15) and (14) in the same way as equations (13) and (12). The new central temperature being θ_0' (an arbitrary value), write L′ for

$$2\left[\lambda'-\frac{\theta_0{}'^5-\theta^5}{\theta_0'-\theta}\right]^{-\frac{1}{2}}.$$

If we give λ' values in the neighbourhood of λ_p, for each value of λ' we shall have a series of values of L′, corresponding to values of θ, for θ between θ_1 and θ_0'. For each value of λ' we can construct a curve connecting θ and L′. The area under each curve is determinate, and by interpolation we can find that value of λ', say λ_p', under which curve the area is equal to ql. We shall arrive in this manner at a solution of equation (15) if λ' be regarded as the unknown.

From the λ_p' curve, as for the λ_p curve, we find the value of θ at the point x, and so the new temperature distribution when the central temperature becomes θ_0'.

The two distributions of temperature determine $\delta\theta$ at the point x, on exposure to radiation, and so $\overline{\delta\theta}$ over the length of the tape. The four equations (12) to (15) are sufficient to determine, for any particular thickness of tape, the mean increment of temperature over the tape when it is exposed to radiant energy.

11. The remaining factors on the right-hand side of equation (23) are readily found. The mean temperatures over the tape, before and after exposure, are given by the curves for λ_p and λ_p' respectively. These temperatures determine γ_M and γ_M', and also, by means of equations (19) and (20), the resistances r_1, $(=r_3)$ and r_1'. Also the resistances r_2 and r_4 are arbitrary, so that equation (22) gives the value of g. The fraction $2\alpha/\gamma_1 mn$ is readily calculated, and the remaining factor $f'(r_1)$ is obtained from the value of C_g. For we have assumed that $C_g=f(r_1)$, so that by differentiating this expression for C_g, and using the values of r_1, r_2, r_3, r_4, proper to the particular thickness of tape, $f'(r_1)$ is determined. R is given by equation (16), and finally, equation (23) gives δz.

12. For each value of n there will be given, by the method outlined, corresponding values of δz and R. It will be shown that, for values of θ_0' between 350° A. and 351° A., δz is proportional to R, when n is constant: so that, for each value of n, δz will be known for a constant R.

Corresponding values of n and δz, for R constant, may then be plotted, and from this curve we expect to find that value of n which makes δz a maximum. In other words, we expect to find a solution of the fundamental equation (1) when throughout the calculations we observe the condition expressed by equation (2).

13. δz *is proportional to* R *when n is constant.*

The general method outlined in paragraphs 9, 10, 11 was applied to a tape of thickness 40×10^{-5} cm., of length 1·6 cm., and width 0·01 cm. Four cases were considered, and θ_0' had values between 350° A. and 351° A., while in every case $\theta_1=290°$ A., $\theta_0=350°$ A. The results of these calculations are set out in Table I.

The final column in Table I. shows that within the limits for θ_0' which have been stated, δz may be assumed to vary as R for any particular thickness of the bolometer tape.

14. *Results of Calculations for Various Thicknesses of Tape.*

The general method of calculation was also applied to nine thicknesses of tape varying from $2{\cdot}423 \times 10^{-5}$ cm. to $583{\cdot}8 \times 10^{-5}$ cm., and in all cases the following values were used:—$\theta_0 = 350°$ A., $\theta_0' = 351°$ A., $\theta_1 = 290°$ A., $m = 0{\cdot}01$ cm., $2l = 1{\cdot}6$ cm. The details of the calculations are not given here, but the principal results obtained from them are set

TABLE I.

θ_0'.	$\delta z \times 10^5$.	$R \times 10^5$.	$\delta z/R$.
351	3·815	38·843	0·0982
350·75	2·855	28·991	0·0985
350·50	1·940	19·233	0·1009
350·25	0·972	9·703	0·1002

TABLE II.

$n \times 10^5$.	$R \times 10^5$.	$\delta z \times 10^5$.	$\delta z/R$.
583·8	307·14	11·547	·0376
284·5	160·52	8·239	·0513
156·1	95·28	6·309	·0662
83·3	59·20	4·916	·0831
40·0	38·84	3·815	·0982
13·67	25·86	2·843	·1099
7·161	23·725	2·517	·1061
3·878	23·07	2·130	·0923
2·423	22·89	1·852	·0809

out in Table II., where the final column shows the galvanometer deflexion, δz, following exposure to unit radiation per unit area of the bolometer tape.

In fig. 1, $n \times 10^5$ has been plotted against $\delta z/R$ for values in the neighbourhood of the maximum indicated by the last column in Table II. From the curve we find that δz is a maximum when $n = 12 \times 10^{-5}$ cm.

In view of the graphical method which has been used throughout, the consequent necessity to approximate, and

the assumptions which have been made, the result may be more convincing if stated thus :—

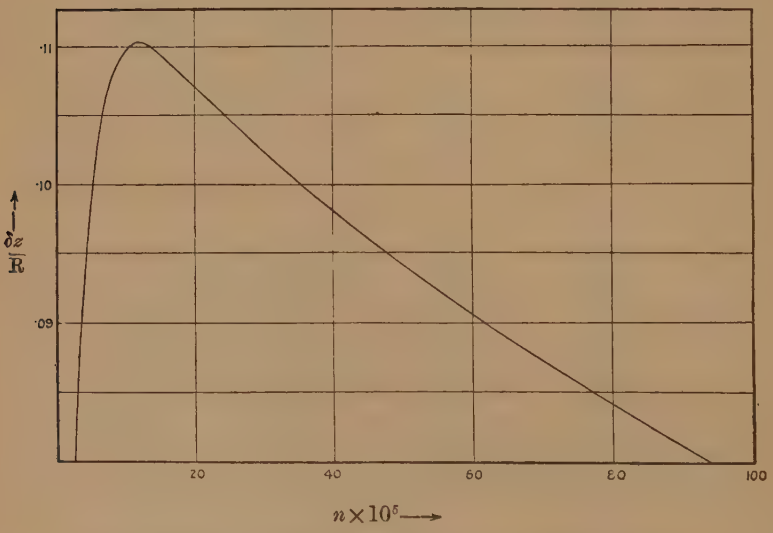
The required solution of equation (1) *is a value of n lying between* $11{\cdot}5 \times 10^{-5}$ cm. *and* $12{\cdot}5 \times 10^{-5}$ cm.

15. *Examination of two Assumptions in the General Method.*

(a) *Resistance variation in concealed tape.*

In paragraph 7 we assumed the resistance r_3 to be constant. When the current i in the exposed tape becomes i' (para. 3, b),

Fig. 1.



Graphical Relation between "$\delta z/R$" and "$n \times 10^5$" to indicate the value of "n" for a maximum "δz."

and the resistance changes to r_1', then $i' < i$. The current in the concealed tape will be increased from i to $C - i'$. The mean temperature of this tape will be increased, and $r_3' > r_3$, if r_3' denote the resistance of r_3 after r_1 has been exposed.

The case where $n = 40 \times 10^{-5}$ cm. was considered in detail, and it was found that the maximum error in the value of r_3 was 0·07 per cent. The errors in $f'(r_1)$ and $g^{\frac{1}{2}}$, factors in the determination of δz by equation (23), were, respectively, less than 0·14 per cent. and 0·15 per cent., and the maximum

error in δz less than 3 in 1000. It was not considered that these errors were sufficient to destroy confidence in the result given in paragraph 14.

(b) *Modification for γ variable.*

Equation (3) was integrated when γ had the value determined by

$$\gamma_1 = \gamma[1+\alpha(\theta-\theta_1)]$$

and

γ_1 = the value of γ for $\theta = \theta_1$.

Corresponding to equation (12), we find

$$gx = \int_0^{(\theta_0-\theta)^{\frac{1}{2}}} \frac{2dy}{[5\theta_1^4+\mu\{2+\alpha(\theta_0-\theta_1)\}+\mu\alpha(\theta-\theta_1)-(\theta_0^5-\theta^5)/(\theta_0-\theta)]^{\frac{1}{2}}}, \quad (24)$$

where

$$\mu = \frac{5}{2}\left(\frac{0{\cdot}24\,i^2}{\gamma_1 m^2 n\sigma}\right), \quad \text{and } q \text{ as before.}$$

Also we find equations similar to equation (24) corresponding to equations (13), (14), (15).

TABLE III.

	i.	i'.	r_1.	r_1'.	$\delta\overline{\theta}$.	$g^{\frac{1}{2}}$.	$f'(r_1)\times10^5$.	$\delta z\times10^5$.
γ constant	0·016455	0·016445	5·368	5·380	0·70	3·114	76·6	3·815
γ variable.....	0·016045	0·016035	5·364	5·376	0·68	3·113	75	3·626

These equations were applied to the case of $n=40\times10^{-5}$ cm., and a comparison is made of values obtained by this method and the previous method (γ constant) in Table III.

Using the method of γ constant, the tabulated quantities are in excess of their true values. We may reasonably infer that this would be true whatever value of n were chosen. Now we do not seek so much to establish the absolute value of δz for a set of values for n as to obtain a comparative set of values of δz. This is what has been done, and we may conclude that no serious error has been introduced in the result given in paragraph 14 by using γ constant as opposed to γ variable.

16. *Summary.*

In this paper an attempt has been made to find, for bolometer tapes of fixed length and width, what thickness of tape would be best to use in measurements of solar radiation. The bolometer tapes form two arms of a Wheatstone's bridge; the ends of the tapes are supposed to be at a constant temperature, 290° A., and the tapes are supposed heated to a central temperature, 350° A., by an electric current. One tape is exposed to solar radiation and the other tape is shielded from the radiation. The balance in the bridge is destroyed, and a sensitive galvanometer shows a deflexion. This deflexion, for a given amount of incident radiation per unit area of tape, is made a measure of the sensitiveness of the bolometric apparatus for various thicknesses of tape. We wish to investigate what thickness of tape would give a maximum galvanometer deflexion.

Nine different thicknesses of tape were examined, and from the results obtained we conclude:

1. That the best tape to use is one whose thickness is between $11{\cdot}5 \times 10^{-5}$ cm. and $12{\cdot}5 \times 10^{-5}$ cm.

2. That where incident radiation raises the temperature at the middle of the exposed tape by 1° C. or less, then, for that particular tape, the deflexion of the galvanometer is proportional to the intensity of the radiation.

The best thickness as here determined is considerably smaller than that in use at the Smithsonian Observatory.

I wish to acknowledge with thanks the assistance I received from Prof. S. Chapman, F.R.S., who suggested the foregoing investigation, and showed me the possibility of using a graphical method for the solution of equations (4) and (8). I wish to offer my thanks also to Prof. E. A. Milne, F.R.S., to whom I am deeply indebted for many suggestions and helpful criticism at numerous stages, as well as for his kindness in reading through the paper and advising important alterations previous to its appearing in the present form.

Newport, Mon.,
18th Jan., 1929.

CXIX. *The Lattice Energy of* LiH *and the Normal Potential of* H^-. *By* R. S. Bradley *.

1. *The Lattice Energy of* LiH.

THE crystal structure of LiH was studied by Bijovet [1]. He found for the internuclear distance 2·01 A.U. This agrees with the value 2·03 A.U. calculated from the moment of inertia of LiH, $6\ 10^{-40}$ gm. cm.^{2}, obtained by Watson [2] from band spectra. Bijovet was unable to decide whether the lattice was ionic or atomic. In this paper the lattice energy will be calculated on the former assumption.

LiH is similar to KCl in that both ions have the same type of electron sheath. The repulsive exponent n for He is determined uniquely as 14·33 and the force constant λ_n as $2{\cdot}35\ 10^{-115}$ [3]. It will be assumed that n for the helium-like ions Li^+ and H^- has not been changed by deformation. The exponent is higher than that usually encountered in crystals and determined from the compressibility. Rashevsky [4], however, has pointed out that the latter method assumes a perfect crystal, whereas the real crystal contains cracks.

The force constants for LiH may be calculated by a modification of the method of Lennard-Jones :

$$\lambda_{Li^+} = \left(\frac{\rho_{Li^+}}{\rho_{He}}\right)^{n-1}\lambda_n, \quad \lambda_{H^-} = \left(\frac{\rho_{H^-}}{\rho_{He}}\right)^{n-1}\lambda_n,$$

where ρ is the atomic or ionic radius, taking $\rho_{Li^+} = {\cdot}78$ [5], $\rho_{He} = {\cdot}945$ [6]. The published values for ρ_{H^-} are discordant. The value taken, 1·40 A.U., lies on the line obtained by plotting ionic radius against nuclear charge for the series He, Li^+, Be^{2+} (·34 A.U.), all of which have He-like sheaths, and agree roughly with Pauling's [7] computation 1·51 A.U. A similar linear relation holds for Ne-like sheaths, etc.

The force constants are then

$$\lambda_{Li^+Li^+} = 1{\cdot}820\ 10^{-116}, \quad \lambda_{H^-H^-} = 4{\cdot}427\ 10^{-113},$$
$$\lambda_{Li^+H^-} = 1{\cdot}445\ 10^{-114}.$$

The lattice energy

$$-U = \frac{1}{2}\frac{N\phi}{J}, \quad J = 4{\cdot}2\ 10^7, \quad N = 6{\cdot}06\ 10^{23},$$

* Communicated by the Author.

where

$$\phi = \frac{e^2 3{\cdot}495}{a} - \frac{2\lambda_{Li^+H^-}A'_{(n-1)} - (\lambda_{Li^+Li^+} + \lambda_{H^-H^-})A''_{(n-1)}}{(n-1)a^{n-1}},$$

a is the internuclear distance, e the electronic charge, n the repulsive exponent, and A' and A'' numbers obtained by interpolation from Lennard-Jones's tables as

$$A'_{n-1} = 6{\cdot}006, \quad A''_{n-1} = {\cdot}1204.$$

The van der Waals's attractive force has been neglected.

Inserting these values we get $-U = 230{\cdot}5$ k.cal. The calculation may be checked by obtaining a value for a. For minimum potential energy we get

$$a^{n-2} = \frac{(\lambda_{Li^+Li^+} + \lambda_{H^-H^-})A''_{(n-1)} + 2A'_{(n-1)}\lambda_{Li^+H^-}}{3{\cdot}495\, e^2},$$

$a = 2{\cdot}18$ A.U., as compared with the experimental value 2·01 A.U.

2. *Comparison with the Value calculated from a Cycle.*

U may be calculated from the cycle

$$\begin{array}{ccc} Li\ (solid) + \tfrac{1}{2}H_2 & \longrightarrow & LiH\ (solid), \\ \downarrow & & \downarrow \\ Li\ (gas) + \tfrac{1}{2}H_2 & \longrightarrow & Li^+ + H^-. \end{array}$$

The energy changes are :

$Li\ (liquid) \longrightarrow Li\ gas$	$-48{\cdot}0$ k.cal.[8]
$Li\ (solid) \longrightarrow Li\ (liquid)$	$-{\cdot}23$ k.cal.
$H_2 \longrightarrow 2H$	$-100{\cdot}1$ k.cal.[9]
$Li\ (solid) + \tfrac{1}{2}H_2 \longrightarrow LiH\ (solid)$.	$+21{\cdot}6$ k.cal.
$Li \longrightarrow Li^+ + e$	$+123{\cdot}5$ k.cal.[10]
$H + e \longrightarrow H^-$	$-1{\cdot}85$ k.cal.[11]

Hence $U = -245{\cdot}2$ k.cal. The discrepancy between this value and the theoretical is not large, and is due to tne uncertainty of ρ_{H^-} and of n in the crystal.

3. *The Normal Potential of* H^-.

Owing to the difference between the lattice energies of LiH and LiF (-245 and -254[12] k.cal. respectively), giving a notable difference in the heat of solution, it is not permissible to use the method of Proskurnin and Kasarnowsky[13] to determine the normal potential of H^-. Instead it will be assumed that the heat of hydration of $H^+ + H^-$ is the same as that of $H^+ + F^-$. This requires a similar identity for ionic entropies[14].

The cell $H^+aq + H^-aq \longrightarrow H_2$ is an interesting oxidation-reduction system, with the half elements

$$H^- \longrightarrow \tfrac{1}{2}H_2 + e, \quad \tfrac{1}{2}H_2 \longrightarrow H^+ + e.$$

The heat of hydration of $H^+ + F^-$ to dilute solution may be obtained from the cycle

$$\begin{array}{ccc} HF & \longrightarrow & H^+ + F^- \\ \downarrow & & \uparrow \\ H^+aq + F^-aq & \longleftarrow & \end{array}$$

The energy changes are:

$$HF \longrightarrow H^+ + F^- \ldots\ldots\ldots -373 \text{ k.cal.}[15].$$

$$HF \longrightarrow H^+aq + F^-aq \ldots +11{\cdot}6 \text{ k.cal.}[16].$$

ΔH for the cell reaction is then calculated from the cycle

$$\begin{array}{ccc} H_2 & \longrightarrow & H^+ + H^- \\ \downarrow & & \downarrow \\ H^+aq + H^-aq & \longleftarrow & \end{array}$$

to be -29 k.cal. Latimer gives $S_0(F^-) = -5$[17]. $S_0(H_2)$ is 29·4. Hence

$$\Delta F_0 = \Delta H - T\Delta S_0,$$

$$= -39{\cdot}3 \text{ k.cal. at room temperatures.}$$

E_0 for the half element $\tfrac{1}{2}H_2 \longrightarrow H^+ + e$ is zero, and hence E_0 for the half element $H^- \longrightarrow \tfrac{1}{2}H_2 + e$ is $-1{\cdot}70$ volts. This is the normal potential of H^-. We may use it to calculate equilibrium concentrations of H^-aq. These will clearly be highest when the concentration of OH^-aq is a maximum.

For the reaction $H^+ aq + H^- aq \longrightarrow H_2$,

$$RT \log_e \frac{P(H_2)}{a(H^+)a(H^-)} = -\Delta F_0 = 39{\cdot}3 \text{ k.cal.},$$

where $P(H_2)$ is the pressure of H_2, and $a(H^+)$ and $a(H^-)$ are activities.

Hence for $P(H_2) = 1$,

$$\log_{10} a(H^+)a(H^-) = -28{\cdot}6.$$

Thus, when the p.h. is about 14 the concentration of H^- is still as low as $10^{-14}-10^{-15}$. It may be increased by using some other oxidation-reduction system, such as

$$Fe^{2+} \longrightarrow Fe^{3+} + e.$$

For the reaction $Fe^{3+} + H^- \longrightarrow Fe^{2+} + \frac{1}{2} H_2$,

$$RT \log_e \frac{a(Fe^{2+})}{a(H^-)a(Fe^{3+})} = 2{\cdot}41 \text{ volt . faradays},$$

when $P(H_2) = 1$.

Hence
$$\log_{10} a(H^-) = \log_{10} \frac{a(Fe^{2+})}{a(Fe^{3+})} - 41{\cdot}6.$$

For $a(H^-)$ to be 1, the ratio $\frac{a(Fe^{2+})}{a(Fe^{3+})}$ would thus have to be $10^{41{\cdot}6}$.

References.

(1) Bijovet, *Rec. Trav. Pays-Bas*, xlii. p. 857 (1923).
(2) Watson, Phys. Rev. xxv. p. 887 (1925).
(3) See, for example, Lennard-Jones in R. H. Fowler's 'Statistical Mechanics' (1929).
(4) Rashevsky, 'Nature,' cxxiii. p. 448 (1929).
(5) Goldschmidt, *Ber. Deut. Chem. Ges.* lx. p. 1263 (1927).
(6) Chapman, Phil. Trans. A, ccxvi. p. 229 (1925).
(7) Pauling, Phys. Rev. xxix. p. 285 (1927).
(8) From vapour pressure of Li in Landolt-Börnstein.
(9) Witmer, Phys. Rev. xxviii. p. 1223 (1926).
(10) Millikan, Proc. Nat. Acad. Sci. xiii. p. 531 (1927).
(11) Pauling, *loc. cit.*
(12) Grimm and Herzfeld, *Zeits. f. Phys.* xix. p. 141 (1923)
(13) Proskurnin and Kasarnowsky, *Zeit. Anorg. Chem.* clxx. p. 301 (1928).
(14) Latimer, J. A. C. S. xlviii. p. 2297 (1927).
(15) Mecke, *Zeits. f. Phys.* xlii. p. 403 (1927).
(16) v. Wartenburg. *Zeit. Anorg. Chem.* cli. p. 313 (1926).
(17) Latimer, J A. C. S. xlviii. p. 2868 (1927).

The University, Leeds,
25 March, 1929.

CXX. *The Electric Arc in Mixed Gases.* *By* F. H. Newman, *D.Sc., F.Inst.P., Professor of Physics, University College of the South-West of England, Exeter* *.

[Plate XXIII.]

1. *Introduction.*

IT has been shown by many experimenters that profound modifications are sometimes observed in the spectrum of a substance when impurities are present, and although most of the investigations have been made on gases in a discharge-tube the effect is also found when the arc is used. Sometimes the spectrum of the impurities is brighter than that of the gas present in bulk, and this is particularly manifest with impurities in the inert gases. Rayleigh † has found that the spectrum of the nitrogen after-glow is modified by the presence of the inactive gases, the effect depending upon the nature of the inactive gas used. Merton and Barratt ‡, employing tubes containing hydrogen and helium at different relative pressures, observed that when the helium was at a comparatively high pressure the lines of both helium and hydrogen appeared with uniform intensity throughout the capillary with an uncondensed discharge, but on placing a condenser and a spark-gap in the electrical circuit the hydrogen lines became much weaker in the centre of the capillary. On the other hand, the mercury lines were intensified with the condenser in the circuit, and they behaved in exactly the opposite manner to the hydrogen lines. Johnson and Cameron § noted a more striking difference in the spectrum of carbon in the presence of argon and helium, for whereas in the latter gas the "comet tail" spectrum and the new line spectrum appear with uncondensed and condensed discharges, respectively, neither of these spectra could be observed under any conditions of excitement when argon was substituted for helium, although the new triplet series of bands could be developed in either gas.

The lines of the Balmer's series are strongly enhanced relatively to the secondary spectrum by very small traces of impurities, and it seems remarkable that any profound

* Communicated by the Author.
† Proc. Roy. Soc. A, cii. p. 453 (1923).
‡ Phil. Trans. A, ccxxii. p. 369 (1922).
§ Proc. Roy. Soc. A, cvi. p. 195 (1924).

influence on the spectrum of a gas can be exerted by impurities which are present in such small quantities that their presence cannot be detected by any characteristic lines or bands in the spectrum. The difficulty of eliminating such impurities as those which give rise to the carbon bands is familiar to all workers with vacuum tubes, and the relative intensities of the lines and bands due to impurities are enhanced enormously as the pressure increases. In addition, the forms in which the impurities appear are also often unusual. McLennan and Shrum *, studying the effect of large admixtures of helium or of neon on the spectrum of oxygen, photographed the line λ 5577, which is identical with the auroral green line λ 5577, and attributed it to some hitherto unknown spectrum of oxygen. Although this line is not obtained in mixtures of pure helium and nitrogen, the presence of the helium greatly enhances the negative bands of nitrogen, but it has little effect upon the second positive group. There is no evidence that a trace of oxygen in a tube containing helium at high pressure would alter the spectrum of the latter very considerably, and, moreover, such an effect is not observed with nitrogen. A strong electric field of atomic origin may displace or resolve a band, and thus an increase of pressure will bring the molecules of a substance into sufficient proximity to produce an electric field strong enough to cause ordinary flutings to appear as continuous bands. The helium atoms have a very small electric field, and therefore, with only a trace of oxygen in helium, the atomic electric forces on the oxygen atoms will be relatively small, and the electron groups occurring under these conditions may give some new radiations.

More recently Keys and Home † have investigated, spectroscopically, the striated discharge in mixtures of (*a*) nitrogen and hydrogen, (*b*) helium and hydrogen, spectrograms being taken of the light emitted by the negative glow and by the striations, respectively. The electronic energies in the different regions of the discharge are interpreted from these spectra to determine the extent of the ionization in different parts of the tube. Their results indicate that the presence of helium in some way prevents the excitation of H_α and H_β in the negative glow, and enhances these lines in the striations. They suggest that

* Proc. Roy. Soc. A, cviii. p. 501 (1925).
† Phys. Rev. xxvii. p. 709 (1926).

the inert gases cause a redistribution of the electronic energy. Terroux * investigated mixtures of argon and hydrogen, and of argon and oxygen, photographing the spectra of the negative glow and of the striated positive column. The change in concentration was found to make little difference in the distribution of electronic energy, and his results seem to indicate that the exciting potentials are correlated with the spectra emitted. Various data suggest, however, that the ionizing potential is not the sole controlling factor in the emission of any particular type of radiation. For example, Keys and Home found the Balmer lines more strongly developed in the striations than in the negative glow, whereas the reverse appears in argon. This, as pointed out by Terroux, may be due to the fact that in argon and hydrogen the ionization potential of argon is slightly less than that of hydrogen, whereas that of helium is one-and-a-half times as great. An electron having a velocity of a little over 15 volts would probably make an elastic collision with a helium atom, and could still ionize a hydrogen atom, but the same electron colliding with an argon atom would ionize the latter and so lose its kinetic energy.

Compton †, investigating the production of atomic nitrogen, found that large currents and high helium pressure favour dissociation of nitrogen, by the action of the excited helium atoms on nitrogen, and with low partial pressures of the latter the arc spectrum of this element is emitted. If the nitrogen is present in large proportion the electrons collide inelastically with nitrogen molecules, and thus lose their energy without exciting the helium. It is only when the proportion of gas is extremely small that the electrons attain the energies required for the helium excitation. Thus Compton has calculated that at 20 mm. helium pressure the nitrogen pressure should be less than 0·01 mm., probably considerably less, in order that most of the electron energy should go directly into the helium. On the other hand, the amount of nitrogen must be sufficient to be appreciable.

The author ‡ has already discussed the variations that occur in the intensity of the spectra of alkali-amalgam vapours when the experimental conditions are varied. For example, with sodium amalgam at temperatures above

* Phys. Rev. xxvii. p. 1242 (1926).
† Phil. Mag. l. p. 512 (1925).
‡ Phil. Mag. xlv. p. 18 (1923); xlv. p. 293 (1923).

200° C. the sodium lines are very intense compared with the mercury lines, whereas at temperatures below 100° C. the mercury lines are predominant, and they were consistently brighter than the potassium lines when a potassium-amalgam was excited. These opposite effects with the two alkalis are difficult to explain. The ionization potential of mercury is greater than that for sodium and potassium, and the mercury vapour pressure is higher at all temperatures. It is evident, therefore, that the ionization potential is not the only critical factor in determining the relative intensity of the spectrum lines in gaseous and vapour mixtures. It was found also that the relative brightness of the individual spectra changed considerably as the nature of the electrical discharge varied. If the vapours of mercury and any one of the alkali metals were both present in the discharge-tube, while the partial pressures were maintained constant, the spectrum of the alkali was always well developed with the ordinary type of discharge, but was completely masked by the mercury lines with the condensed discharge. All of the alkali metals have lower resonance and ionization potentials than mercury, so that although the amount of mercury present may be comparatively great yet the electrons during their mean free paths are more likely to acquire the energy necessary for ionization of the alkali atoms. As a result the concentration of the luminous sources may be great enough to exhibit the alkali spectrum. With the condensed discharge, and consequent increase in the electrical energy, a greater proportion of the mercury atoms will be ionized because the colliding electrons will attain higher energy during the mean free paths. The mercury lines become very bright. At the relatively high pressures employed the mean free path has a small value, and it is unlikely that the ionizing energy can be obtained by impact alone; more probably it is acquired chiefly by radiation absorption.

Practically no work on the relative intensity of spectra excited by means of the arc has been done, but the author * has shown that when an arc is passed through hydrogen which has not been dried the Balmer lines are not accompanied by any continuous spectrum, whereas with dry gas the secondary spectrum, together with a continuous spectrum, are both intense. It is evident, therefore, that traces of foreign vapours will affect the arc spectra of gases and

* Phil. Mag. vi. p. 807 (1928).

vapours, and in most cases the changes produced may be expected to resemble those made by the uncondensed electrical discharge.

2. *Experiments.*

One of the most convenient methods for investigating the arc in various atmospheres is that described by the author *, in which a temporary discharge is sent between two electrodes, a potential difference being applied between one of these electrodes and a third one. This arrangement starts and maintains the arc, and provided that it is not allowed to continue for any length of time, the radiation emitted is that characteristic of the gas, few iron lines appearing. In this way very large currents may be sent through the gas. In the present work, after the tube had been exhausted to 10^{-5} cm. pressure, the gas under examination was admitted in small doses, and thus any required pressure could be obtained. For some experiments the gas was mixed with a little water vapour, while in others it was carefully dried by allowing it to stand over phosphorus pextoxide for several hours. Helium and neon were tested separately, each gas being 98 per cent. pure and containing 2 per cent. of the other gas as an impurity. From the results obtained it was evident that the impurity had little if any effect upon the phenomena occurring, so that the impurity was not removed.

An arc such as described above can be started in hydrogen at low pressure and also in the residual gases remaining in the tube after exhaustion, but great difficulty was experienced in striking the arc in helium and neon atmospheres at all pressures varying from 10^{-3}–1 mm. Even when the arc was started it could not be maintained, but if a small bead of borax was fused on to the cathode this difficulty was eliminated and the arc started and persisted as in hydrogen. The characteristic radiations associated with helium and neon were absent, the core of the arc being brilliant white in colour with a surrounding column of yellow-coloured radiation which, when examined, showed only the D lines. The Balmer lines were present together with the CN bands and many other lines which have not been completely classified. The helium and neon spectra could be detected when the dried gas was used, but even in this case the lines were faint compared with the other lines and bands. If the arc was interrupted, and the potential difference re-applied across the

* *Loc. cit.*

electrodes immediately after the interruption, a blue glow appeared in the vicinity of the cathode, and persisted for a short time. This glow is attributed to the fact that in the immediate neighbourhood of the electrode the potential fall is sufficient to speed up the residual ions so that they attain energy equivalent to the ionization potentials of the gases present. The glow was faint and existed for such a short interval of time that it was not possible to examine it spectroscopically.

The luminous radiation from the arc was photographed through a quartz window by means of a quartz spectrograph, special rapid panchromatic plates being used. An examination of the results obtained with helium which had not been dried showed that the helium lines were very faint, the Balmer lines from hydrogen present as an impurity being much stronger. Mercury lines, especially λ 2537, and the ammonia bands were prominent, but the CN bands, particularly those at λ 3883 and λ 3590, were by far the most intense lines on the plates. The actual percentage of nitrogen, carbon monoxide, carbon dioxide, etc. present in the tube must have been exceedingly small, and when the arc was sent through these residual gases the CN bands did not appear, so that helium and neon cause emission of the bands even when the amounts of nitrogen and carbon compounds present as impurities are very small. A careful examination of the plates did not reveal any of the nitrogen arc lines such as Compton found when helium was mixed with a small percentage of nitrogen. The striking difference between the spectra of the residual gases and of these gases mixed with helium and neon is seen in Pl. XXIII.

When the helium was replaced by neon which had been thoroughly dried, the Balmer lines were relatively faint compared with the neon ones; otherwise there was very little difference. If the arc were allowed to burn for a short interval the electrodes become very hot and the iron lines appeared. These lines, however, had different relative intensities compared with the results obtained with the iron arc in air. In particular it was noted that the group of lines λ 2382–λ 2411 were intense if water-vapour was absent.

The faintness of helium and neon lines in this type of arc is interesting, especially as the ordinary electric discharge through these gases gives the characteristic spectra associated with them. The CN bands which are prominent may be excited thermally at a temperature of 2100° C. and correspond to electronic resonance potential of 3·18 volts. The

equilibrium concentration of CN may be expected to increase with temperature and to become a relatively abundant molecular species. Thus in the carbon arc, which has a temperature of about 4000° C., the bands are of great intensity, and in the present type of arc, although it is not at such a high temperature, it has a value sufficiently great to vaporize the iron electrodes after a few seconds, so that conditions are favourable for the formation of CN. Since the low resonance potential indicates a low ionization potential, it appears that the CN is ionized by the colliding electrons of comparatively small energy. Helium possesses minimum excitation states of 19·73 and 20·56 volts, the ionization potential for atoms of this gas being 24·5 volts. To produce the Balmer lines from molecular hydrogen requires 15·5 volts and the negative bands of nitrogen require 17·75 volts, so that at higher gas pressures the chance of electrons acquiring the ionizing energy is least for helium and greatest for CN. The helium atoms increase by elastic collisions the total path of the electrons through the tube and thus increase the chance of collision with a molecule of CN, and it is only when the proportion of nitrogen, hydrogen, carbon dioxide, etc. is extremely small that the electrons attain the energy necessary for excitation of the helium. As the helium gas pressure is increased the amount of nitrogen, etc. must be diminished if most of the electrons are not to lose their energy directly to the nitrogen. Although the actual amount of CN produced by the high temperature of the arc would of necessity be small the percentage ionized should be high, since the probability of two ionized CN molecules colliding would be less than the chances of one meeting with a helium atom. During collisions between helium atoms in the excited state and molecules of CN the excited helium atoms may return to their normal state without radiation, the energy, which would appear as radiation if the atom were to pass spontaneously from a higher stationary state to a lower one, ionizing the CN molecules, and the CN bands accordingly appear.

The cathode potential fall, although not measured in the present arc, is undoubtedly sufficient to ionize any of the gaseous molecules and atoms present, and this cathode fall is reduced by fusing the borax on the electrode. When it is reduced below a value of 120 volts, approximately, it is not sufficient to produce ionization of the molecules and the arc will not start.

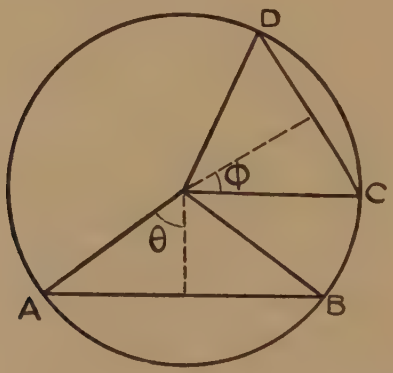
CXXI. *Note on a Geometrical Radiation Problem.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the February issue of the Philosophical Magazine, Prof. E. A. Milne has treated the problem of the radiation reaching one circular disk from another. This problem was one of those treated by J. H. Lambert in his 'Photometria sive de mensura et gradibus luminis, colorum et umbræ' (1760), and the formula is to be found on p. 100 of the original work or on p. 81 of the German translation (Ostwald's 'Klassiker,' Nr. 31).

Fig. 1.



Prof. Milne also refers to the fact that when the disks are of equal radius the radiation reaching one disk from the other is less than that which would reach it from an infinitely large disk, in the ratio $\tan^2\frac{1}{2}\theta$. He states that no simple method of proof of this result has suggested itself. The result is, however, quickly obtained from the well-known principle that a disk, the edge of which forms a circle on a sphere, receives equal amounts of flux from equal areas of the sphere surface irrespective of the positions of those areas*. Thus the radiation reaching AB (see fig. 1) from the area CD is less than that reaching it from the whole area BCDA in the ratio of the spherical area cut off by the disk CD to the spherical area BCDA, *i.e.*, in the ratio

$$(1-\cos\phi)/(1+\cos\theta)=(\sin^2\tfrac{1}{2}\phi)/(\cos^2\tfrac{1}{2}\theta).$$

* See, *e.g.*, Phys. Soc. Proc. xxxii. p. 59 (1920).

In the special case when the disks are equal this reduces to Prof. Milne's expression, $\tan^2\frac{1}{2}\theta$. It is to be noted that parallelism of the disks is not necessary. All that is postulated is that the edges of the two disks shall form small circles of the same sphere.

Yours truly,

JOHN W. T. WALSH.

The National Physical Laboratory,
Teddington, Middlesex,
4th April, 1929.

CXXII. *Uniformly Diffused Light through Two Apertures.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the February issue of the Philosophical Magazine, Dr. A. Gerschun has pointed out that the above problem, solved by Prof. L. F. Richardson * as an example of his method of computation by "deferred approach to a limit" †, has an analytical solution which is, in fact, a special case of the solution of a more general case given in Herman's 'Treatise on Geometrical Optics.' The amount of flux that will go in series through two apertures forming opposite faces of a cube of side l can thus be shown to be equal to

$$0{\cdot}627768\, l^2\mathrm{B},$$

where B is the brightness of the side admitting the flux. It is of interest to notice that, since the total flux admitted by this side is $\pi l^2\mathrm{B}$, the amount reaching each of the four adjacent sides is

$$\begin{aligned}&\tfrac{1}{4}(\pi - 0{\cdot}627768)\, l^2\mathrm{B}\\ &= 0{\cdot}628456\, l^2\mathrm{B}.\end{aligned}$$

Thus the interesting result is obtained that, to 0·1 per cent., each of the five sides receives $\frac{1}{5}\pi l^2\mathrm{B}$.

It is, perhaps, of interest to point out that the general problem is of considerable practical importance in illuminating engineering for calculating the amount of light which reaches the walls of a rectangular light-shaft in a building,

* Phil. Mag. vi. p. 1019 (Nov. 1928).
† Phil. Trans. Roy. Soc. A, ccxxvi. p. 299.

assuming the shaft to be open at the upper end to a sky of uniform brightness. If reflexions from the walls be neglected, it is clear that the flux reaching an elementary strip of the walls of height dc, situated at a distance c below the top of a shaft of sides a, b, is equal to the first differential with respect to c of the expression given by Herman, viz.,

$$B\Big[c^2\log\frac{(c^2+a^2)(c^2+b^2)}{c^2(c^2+a^2+b^2)}+2a(c^2+b^2)^{\frac{1}{2}}\tan^{-1}\frac{a}{(c^2+b^2)^{\frac{1}{2}}}$$
$$-2ac\tan^{-1}\frac{a}{c}+2b(c^2+a^2)^{\frac{1}{2}}\tan^{-1}\frac{b}{(c^2+a^2)^{\frac{1}{2}}}-2bc\tan^{-1}\frac{b}{c}\Big].$$

Yours very truly,
JOHN W. T. WALSH.

The National Physical Laboratory,
Teddington, Middlesex,
4th April, 1929.

CXXIII. *Frequency Variations of the Triode Oscillator.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN the January number of the Philosophical Magazine, Lieut.-Col. K. E. Edgeworth again attempts to prove that his paper read before the Institute of Electrical Engineers (Wireless Section) on the 6th of January, 1926, is in many respects similar to my paper under the above title in the Philosophical Magazine for November 1927 ; and he repeats that, "So far as they cover the same ground, the experimental results appear to be in agreement and the explanations offered are substantially the same." In his latest note Edgeworth seeks to prove that my equation,

$$p^2=\frac{1}{L_1C_1+k_1k_3(L_1L_2-M^2)}, \quad . \quad . \quad . \quad . \quad (1)$$

which is fundamental to the work, is already contained in his paper in the form :

$$f=\frac{1}{2\pi\sqrt{L_1C_1}}\left\{1+\frac{1}{2A}\left(R_1-\frac{R_2C_2}{C_1}-\frac{R_1R_2C_2}{2L_1}\right)\right\}. \quad (2)$$

Incidentally, it may be mentioned that this latter equation appears not in Edgeworth's paper, but at the end of his reply to the discussion, and that the method by which it is

derived is not indicated. Coupling this equation (2) with a third equation,

$$R_2C_2 = R_4C_2 + \frac{L_2\sigma}{G}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which he states to be given in the body of his paper immediately after equation (18), Edgeworth derives the equation:

$$f = \frac{1}{2\pi\sqrt{L_1C_1}}\left\{1 - \frac{\sigma L_2}{2AC_1G}\right\}. \quad . \quad . \quad . \quad (4)$$

He now makes the assumption that in my equation (1), $k_1k_3\,(L_1L_2 - M^2)$ is small compared with L_1C_1, and then shows that equations (1) and (4) are identical. Edgeworth then states that "The identity of these two equations provides a formal proof that the frequency variation investigated by Martyn is the same as the frequency variation of the first type discussed in my paper. . . . Most of the points discussed in Martyn's first paper . . . can be derived from any of the above equations with equal facility." How completely fallacious is this point of view the following considerations prove.

(1) The frequency variations examined in my paper, both experimentally and theoretically, *are extremely large and extend over several octaves.* Hence Edgeworth's equation, which, as he says himself, is only valid for small variations of frequency, cannot possibly be made to apply thereto. It is absolutely impermissible for Edgeworth to take my equation (1), assume that $k_1k_3(L_1L_2 - M^2)$ is small compared with L_1C_1, and then show that my equation can be transformed into his equation (4) because $k_1k_3(L_1L_2 - M^2)$ is usually several times greater than L_1C_1 in my work. Hence Edgeworth has really proved that my equation (1), which was derived to explain large frequency variations, can also explain small variations of frequency such as were obtained by Edgeworth—a fact which is, *ab initio*, obvious. But he has completely failed to prove his contention that his own equation (4) can explain the large frequency variations which I obtained.

(2) Edgeworth uses the equation (3) in "proving" the identity of equations (1) and (4) above. This equation is stated to appear in his paper after equation (18). On consulting his original paper at the place mentioned, I find the following equation:

$$R_2C_2 = R_4C_2 + \frac{L_2}{G}.$$

Where the σ has come from in equation (3) is a mystery, but certainly without its appearance not even an attempt at "proof" of the identity of our equations could be made.

There is no doubt that for frequency variations of any importance equation (1) supplies the complete explanation, and that the causes of variation theoretically considered by Edgeworth are of minor importance, as pointed out in my last note.

Yours faithfully,
D. F. Martyn, Ph.D.

CXXIV. *Notices respecting New Books.*

An Introduction to Crystal Analysis. By Sir William Bragg, K.B.E., D.Sc., F.R.S. [Pp. vii+168, with 105 figures.] (London: G. Bell and Sons. 1928. Price 12*s.* net.)

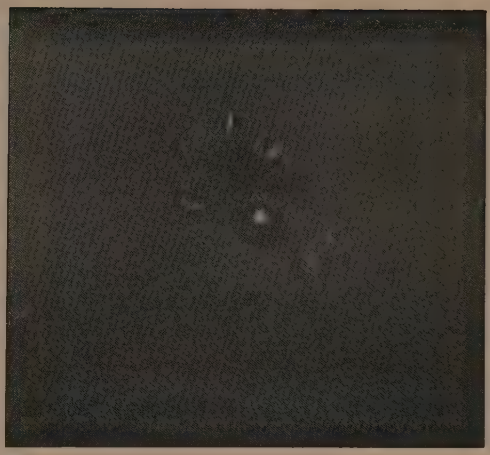
The Structure of an Organic Crystal. By Sir William Bragg, K.B.E., D.Sc., F.R.S. [Pp. 32, with 10 figures.] (London: Longmans, Green and Co. 1928. Price 1*s.* 6*d.* net.)

The application of X-rays to the study of crystals has given valuable information about the structure of crystals, both inorganic and organic, and has proved of great assistance to the chemist, the metallurgist, and the crystallographer. In the first of the above volumes, an excellent account is given of the principles underlying the methods of crystal analysis, of the various experimental arrangements employed, and of some of the results obtained. One chapter is devoted to the various types of space groups or crystal arrangements. The examples include simple inorganic crystals of the atomic type, such as the diamond, and of the ionic type, such as calcium fluoride; somewhat more complex crystals such as calcite; complex crystals such as the alums and various organic substances; and metal crystals. The volume throughout is characterized by the author's gift of clear, simple exposition, and forms an excellent introduction to the new subject.

The second volume contains the Fison Memorial Lecture, 1928, delivered at Guy's Hospital Medical School. It deals with the structure of organic crystals as deduced from X-ray analysis and the bearing of the results upon the structure arrived at by chemists from purely chemical considerations.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

No. 23

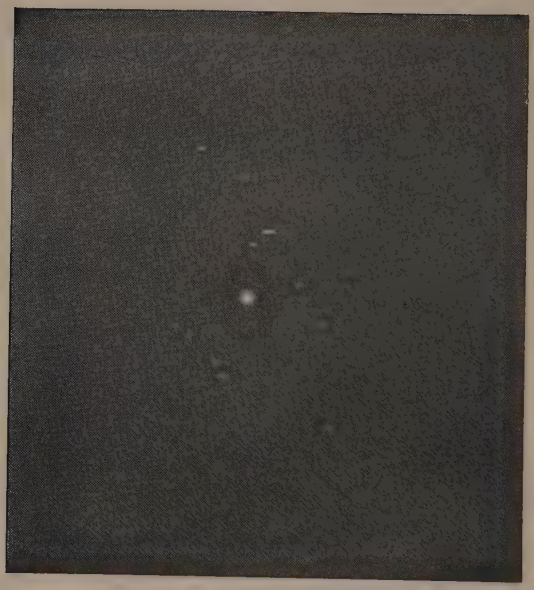


104 tons sq. in.

No. 24.

1 ton/sq. in.

No. 21.



88 tons sq. in.

No 22

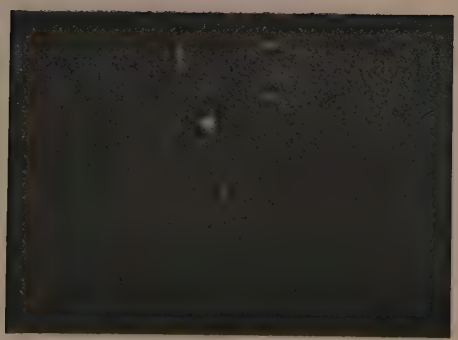
97 tons sq. in.

Laue Diagrams of Tungsten Crystal W.C. 1.

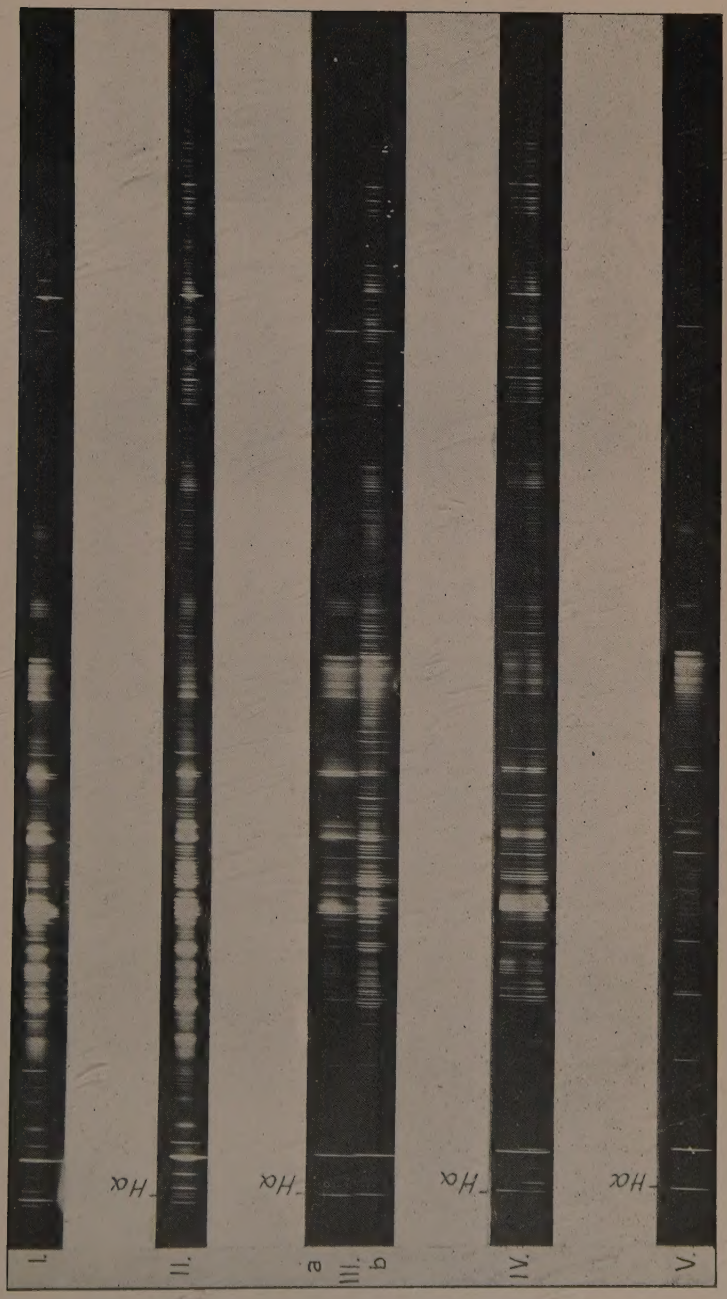
No. 23

104 tons sq. in.

No. 24.



1 ton/sq. in.



SPECTRA OF ARC THROUGH MIXED GASES.

I. Helium. Water-vapour present. II. Helium. Dry.
III. (*a*) Neon. Water-vapour present; (*b*) Neon with Iron lines.
IV. Neon. Dry. V. Residual gas spectrum.